Options for Treatment of Ammonia in Landfill Leachate

by

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Abstract

Treatment of landfill leachate is often needed to remove ammonia nitrogen (free ammonia and dissolved organic nitrogen) because high concentrations are known to negatively impact on waterways and the wastewater treatment process. The objective of this study was to examine ways to reduce ammonia nitrogen in landfill leachate. The methods explored were coagulation–flocculation, adsorption and system integration methods. For coagulation–flocculation treatment: jar test experiments explored the best coagulant, effective dose, pH control, mixing regimes and the use of polyelectrolytes. Three conventional coagulants – anhydrous ferric chloride, hexahydrate ferric chloride and aluminium sulfate – were examined, alongside three commercial cationic polyelectrolytes. The best coagulant was anhydrous ferric chloride, and the coagulant dosage and pH were found to be very crucial. Anhydrous ferric chloride showed removal of about 20%, 29% and 77% of ammonia nitrogen, Chemical Oxygen Demand (COD) and colour respectively at an optimum dose of 2,000 mg/L at pH 7. The mixing regimes and polyelectrolyte additions were insignificant in ammonia nitrogen removal.

Sorption using local soils (type A, B, C and D) and zeolite was also studied. The four local soils were equally ineffective in removing ammonium from landfill leachate (< 5.0% removal); in contrast, zeolite was somewhat effective (23%).

Two system integrations were analysed: one between coagulation–flocculation and biological nitrification, and the other between adsorption and coagulation–flocculation. Obstacles encountered in biological nitrification made it challenging to draw a conclusion as to its potential. In contrast, the integration of an adsorption method with coagulation–flocculation achieved maximum reductions of ammonia nitrogen, COD, colour and turbidity of 36%, 47%, 96% and 85% respectively from landfill leachate. This treatment, however, still produces landfill leachate with high (1,450 mg/L) ammonia nitrogen concentrations.

Acknowledgement

To begin with I would like to give all the glory to Jesus Christ my God for giving me life, good health and strength throughout my research. Lord You are good all the time. The gratitude is also extended to Prophet TB Joshua and The SCOAN ministry for their endless prayers throughout my research.

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"Better is not good enough, the best is yet to come"

Emmanuel! : God with us (John 1:9)

Table of Contents

List of Figures

List of Tables

Terminologies

Symbol	Description	Unit
$\mathcal{A}$	Specific area per unit volume of the adsorbent	m^2/kg or m^2/g
C_e	Ammonia nitrogen concentrations at equilibrium	mg/L
CEC	Cation exchange capacity	meq/100 g
C_i, C_o	Initial concentrations of ammonia nitrogen, COD, turbidity, SS and colour	mg/L
C_f	Initial concentrations of ammonia, COD, turbidity, SS and colour	mg/L
Du_s	Change in soil moisture	% or $m^3.m^3$
Du_w	Change in the moisture content of the solid waste components	% or $m^3.m^3$
ET	Actual evaporation losses	mm day^{-1}
Feed	A sample of wastewater to be treated that is added to a microbial culture for biological processing in a laboratory setting	
L	Leachate production	Litres per hectare per day
N	Normality of sulfuric acid (H_2SO_4)	meq/L
n_s	Surface concentration	mol/m^2
P	Precipitation	ml
q_e	Equilibrium adsorption of ammonium nitrogen adsorption	mg/g
R	Surface runoff	$kg/m^2/s$
R1	Experiments conducted on coagulated leachate substrates	-
R2	Experiments conducted on raw leachate.	-
Type A	Very stable (slope angle ratio of 1:1) cohesive soils having an unconfined compressive strength greater than 1.5 tons per square foot	-
Type B	Less stable (slope angle ratio of 3/4:1) cohesive soils having an unconfined compressive strength between 0.5 and 1.5 tons per square foot	-
Type C	Soils collected from a water supply pond having a slope angle ration of 1-1/2:1 unconfined compressive strength less than 0.5 tsf	-
Type D	Soils collected from a stormwater siltation pond	-
V	Volume of leachate solution	litre
W	Mass of leachate solution	grams
α_{AB}	Separation factor	-

Abbreviations

AASHTO	**American Association of State Highway and Transportation Officials**
ASTM	American Society for Testing Material
BOD5	5-day biological oxygen demand
CEC	Cation exchange capacity
CCC	Christchurch City Council, the local territorial authority
COD	Chemical oxygen demand
Cu, Cr	Copper, Chromium
EPA	Environmental Protection Authority
$FeCl_3$	Anhydrous ferric chloride
$FeCl_3.6H_2O$	Hexahydrate ferric chloride
HCL	Hydrochloric acid
Mg	Magnesium
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
MSW	Municipal Solid Waste
NaOH	Sodium hydroxide
NH_3-N	ammonia nitrogen
Ni	Nickel
NO_2^-	Nitrites
NO_3 –N	Nitrates
OH^-	Hydroxide ion
Pb	Lead
Rpm	Revolutions per minute
SS	Suspended Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TKN	Total Kjeldahl Nitrogen
USDA	United States Department of Agriculture (Natural Resources Conservation Services)
VOCs	Volatile organic compounds
XOC	Xenobiotic organic compound
Zn	Zinc
Zp	Zeta potential

CHAPTER 1. Introduction

1.1 Background

Landfilling has become an important part of the system for managing municipal solid wastes (MSW) in many countries due to its lower operational and maintenance costs (Shivayogimath & Chandrakant, 2013; Syafalni et al., 2012). Worldwide, MSW has been reported to have increased tremendously in past decades. For example, according to a report by Qasim & Chiang (1994), over 180 million tons of MSW was generated in 1988 in the United States. Moreover, by 1995 the generation of MSW increased to 200 million tons, and by the year 2000 to 216 million tons. Developing countries have also experienced a trend of increasing MSW resulting from the growth in urbanisation (Diaz, Eggerth, & Savage, 2007). According to the World Bank (2012), an increase of up to 4.3 billion urban residents has been anticipated in developing countries by 2025. This urbanisation growth is also anticipated to generate about 2.2 billion tons of MSW. The MSW generated by developing countries is mostly composed of food waste prepared from base ingredients, organic nitrogen being common in much of this food waste (Mihelcic & Zimmerman, 2013). This increased MSW also results in the production of landfill leachates rich in ammonia –the concern in this study.

Landfill leachate is a liquid formed by the degradation of the organic solid waste fraction that combines with rain as it infiltrates the compacted waste and reaches the bottom of the landfill (Poveda, Yuan, & Oleszkiewicz, 2016; Shivayogimath & Chandrakant, 2013). Most MSW landfill leachates are considered dangerous, as they contain large amounts of inorganic salts, organic matter, chlorinated organics, heavy metals and ammonia nitrogen (Sang, Sun, Chen, & Liang, 2008; Shivayogimath & Chandrakant, 2013; Tsatsi, Zouboulis, Matis, & Samaras, 2003). Leachate often has higher concentrations of ammonia, COD, colour and turbidity than typical municipal wastewater. According to Rui, Daud, and Aziz (2012), the concentration of ammonia nitrogen in municipal landfill leachate could reach several thousand mg/L, significantly higher than the 1 mg/L aquatic toxicity limits. In view of this, landfill leachate has been identified as a potential source of environmental contamination in ground and surface waters (Tsatsi et al., 2003), so prompting this study.

1.2 Leachate problems in the environment

The problems related to ammonia in leachate are as follows:

- High concentrations of ammonia negatively impact on wastewater treatment processes and reduce the quality of the effluent preventing it from meeting the discharge standards (Poveda et al., 2016).
- The ammonium ion has an oxygen demand as it changes to nitrates hence results in dissolved oxygen depletion from the surrounding water bodies.
- Ammonia concentrations higher than 1 mg/L are very toxic to aquatic life (Aziz, Adlan, Zahari, & Alias, 2004)
- Nitrogen is a nutrient and in excess contributes to eutrophication in the surrounding water bodies.

Landfill leachate with high ammonia concentration has proven challenging for municipalities to manage. It would be very beneficial, therefore, to treat the landfill leachate to remove ammonia nitrogen (meaning free ammonia and dissolved organic nitrogen) prior to discharge into municipal wastewaters or to the environment. Moreover, pretreating landfill leachate can also facilitate recirculation of leachate and so reduce treatment costs.

1.3 A need for research

There is a need for landfill leachate pretreatment methods that are effective, simple in operation, low in capital cost and that result in reduced operational costs. According to previous studies, pretreatment for ammonia nitrogen proved challenging and, therefore, new ways are needed. Consequently, this research explored closely the potential for, and limitations on, ammonia nitrogen removal via low technology options.

1.4 Research objectives

There are four objectives:

1. to investigate the removal of ammonia nitrogen from landfill leachate using the physical-chemical technique of coagulation–flocculation, including the use of conventional coagulants (anhydrous ferric chloride, hexahydrate ferric chloride, aluminium sulfate) alongside the effect of polyelectrolytes addition
2. to investigate an adsorption technique for ammonia nitrogen removal from landfill leachate, using four local soils (silt and calcareous soils) and zeolite soil,
3. to investigate the removal of ammonia nitrogen through a system integration between coagulation–flocculation and biological nitrification that converts it into nitrates
4. to investigate the removal of ammonia nitrogen through a system integration between adsorption and coagulation–flocculation.

The key activities undertaken include, but are not limited to, the following:

- characterise landfill leachate for levels of ammonia nitrogen and other contaminants.
- reproduce results of ammonia removal from previous research.
- determine the efficiency of coagulation–flocculation method in removing ammonia nitrogen from landfill leachate. Thus, identifying the coagulants and polyelectrolytes that can achieve the best removal of ammonia nitrogen.
- examine and analyse the performance of anhydrous ferric chloride, hexahydrate ferric chloride, aluminium sulfate, and polyelectrolytes in removing ammonia nitrogen from the leachate.
- vary the pH and mixing regimes and examine their effect on leachate treatment.
- examine and analyse the interaction between coagulants and polyelectrolytes in treating leachate.
- compare the results of the percentage removal of ammonia nitrogen, COD and turbidity.
- study the adsorption technique using zeolite, silt and calcareous soils (types A, B, C, and D) and compare the results of ammonia nitrogen removal.
- study the system integration between coagulation–flocculation and biological nitrification that converts ammonia nitrogen into nitrates using nitrifying microbes from activated sludge.
- study the system integration between adsorption and coagulation–flocculation that promotes particle destabilisation and flocculation to remove ammonia nitrogen.

CHAPTER 2. Literature review

2.1 Overview

The literature review for this research focuses on four key areas. It starts with an insight into landfilling as the most practiced solid waste management technique in both developed and developing countries. This first part also explains how the landfill leachate is generated, its characteristics and the emphases on nitrogen and ammonia, and their impact on the environment. The second part highlights the existing ammonia pretreatment methods for landfill leachate, and their weaknesses. Thirdly, coagulation–flocculation, adsorption and nitrification phenomenon are explained, including the conditions required. Lastly, a general review of previous studies that focused on treating ammonia nitrogen from landfill leachate using coagulation–flocculation has been included.

2.2 Municipal solid waste management in the developed and developing countries

Historically, solid wastes have proved to be one of the most pressing environmental issues for both developed and developing countries (Diaz et al., 2007). Some of these problems are attributed to a tremendous increase in solid waste generation, inappropriate solid waste collection, unacceptable dumping, and pollutants from the solid waste. Generation of municipal solid waste (MSW) has been reported to have increased tremendously in recent decades worldwide, especially in developed countries. In 2011 the EPA reported a more detailed increase in quantities of MSW generated in the U.S. from 1960 to 2010 (Mihelcic & Zimmerman, 2013) as presented in Table 2-1. This shows a dramatic increase of MSW generation rates from 0.44 to 0.74 Mg/person/year between 1960 and 2010. The generation of more MSW threatens public health and the environment. However, in dealing with management of MSW, the developed countries such as the United States, have been using landfilling as their most common method of MSW management, as shown in Table 2-1.

Table 2-1: MSW Quantities in U.S (Mihelcic & Zimmerman, 2013)

	Mg per Person per Year						
	1960	1970	1980	1990	2000	2005	2010
Generation	0.44	0.54	0.61	0.76	0.78	0.77	0.74
Recycling	0.03	0.04	0.06	0.11	0.17	0.18	0.19
Composting	Neg.	Neg.	Neg.	0.01	0.05	0.06	0.06
Incineration	0	0	0.01	0.11	0.11	0.1	0.09
Landfill	0.42	0.5	0.54	0.53	0.45	0.43	0.4

1 These quantities exclude construction and demolition debris and wastewater plant sludge.

2 This includes small quantities of waste incinerated without energy recovery and does not include wastes produced during recycling, composting, and incineration (eg, ashes).

Note. Retrieved from Environmental Engineering book. Copyright 2013 by Mihelcic and Zimmerman. Reprinted by permission.

Moreover, developing countries for the last three decades have also experienced a trend of urbanisation growth more than the developed countries, as shown in Figure 2-1 (Khatib, 2011). This growth has led to serious urban area population growth. In view of these, an increase of up to 4.3 billion of urban residents who will be generating about 2.2 billion tonnes of MSW has been anticipated in developing countries by 2025 (World Bank, 2012).

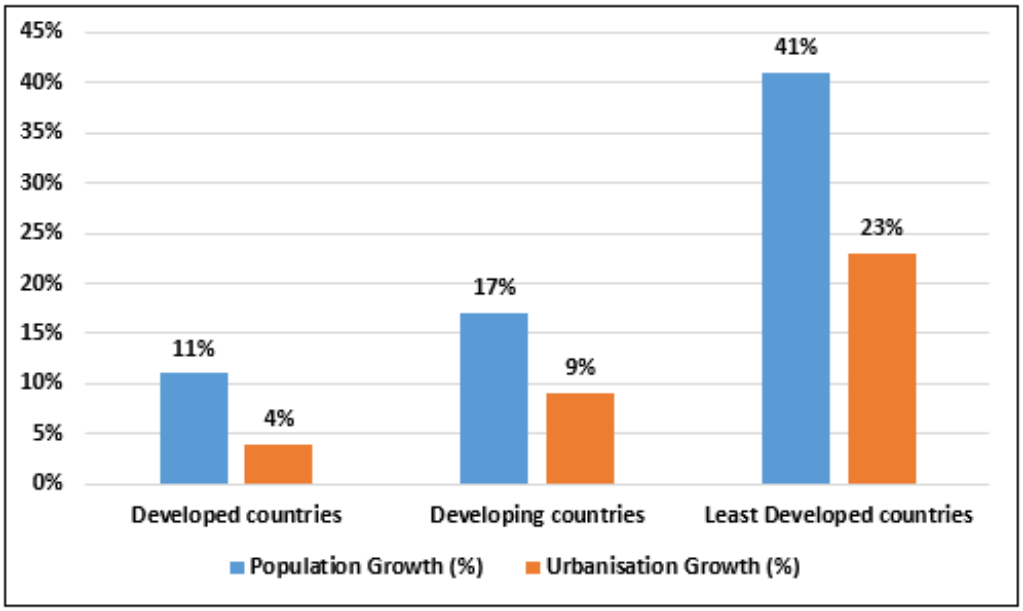


Figure 2-1: 1990 – 2010 population and urbanisation growth (Khatib, 2011)

Copyright 2010 by Khatib.

In dealing with the increase in MSW, some developing countries have been using landfills as their solid waste management method. However, most communities for economic reasons are still using dumps, and this method has a huge impact on health, environment, and economy (World Bank, 2012).

2.2.1 Nature of municipal solid waste in developed and developing countries

MSW is a collection of urban waste characterised by their source and nature, which vary from country to country or by region (Diaz, Savage, Eggerth, & Golueke, 1996; Mihelcic & Zimmerman, 2013). MSW can be divided into organic or inorganic waste. Organic waste can also be putrescible (decomposes rapidly), fermentable (decomposes rapidly without odour) and non-fermentable (Diaz et al., 1996).

a. Municipal solid waste and their sources

MSW materials are considered waste when they are no longer of any value and are ready for disposal (Diaz et al., 1996; Mihelcic & Zimmerman, 2013). These includes waste from households (single and multifamily residences), municipal services, institutional, commercial, agricultural, industrial, construction and demolition. Table 2-2 shows sources of solid waste in the developed world including their percentages as found in MSW. The materials in the MSW include plastic and paper generated at home, food wastes from cafeteria, industry ashes, cut grass and leaves from parks, medical wastes from hospitals, and construction site demolition debris (Diaz et al., 1996; Mihelcic & Zimmerman, 2013). Figure 2-2 shows an example of materials found in MSW by percentages, as generated in 2010 in the United States.

Table 2-2: Developed Countries Municipal Solid Waste Sources and Their Typical Percentages. (Adapted from Mihelcic and Zimmerman, 2013).

Source	**Examples**	**Comments**	**Typical percentage of MSW (%)**
Residential	Detached homes, apartments	Food wastes, garden/yard wastes, paper, plastic, metal, glass, household hazardous wastes.	30–50
Commercial	Stores, restaurants, office buildings, motels, auto repair shops, small businesses	Same types as above, but more variable from source to source. Small quantities of specific hazardous wastes.	30–50
Institutional	Schools, hospitals, prisons, military bases, nursing homes	Same types as above, variable composition between sources.	2–5
Construction and demolition	Building construction or demolition sites, road construction sites	Concrete, metal, wood, asphalt, wallboard and dirt predominate. Some hazardous wastes possible.	5–20
Municipal services	Cleaning of streets, parks and beaches, water and wastewater treatment grit and sludge, leaf collection, disposal of abandoned cars and dead animals	Waste sources vary between municipalities.	1–10
Industrial	Light and heavy manufacturing, large food processing plants, power plants, chemical plants	Can produce large quantities of relatively homogeneous wastes. Can include ashes, sands, paper mill sludge, fruit pits, tank sludge.	Not MSW
Agricultural	Cropping farms, dairies, feedlots, orchards	Spoiled food,	Not MSW
Mining	Coal mining, gold mining, oil/gas exploration or extraction	Can produce vast amounts of solid waste needing specialised management.	Not MSW

Note.

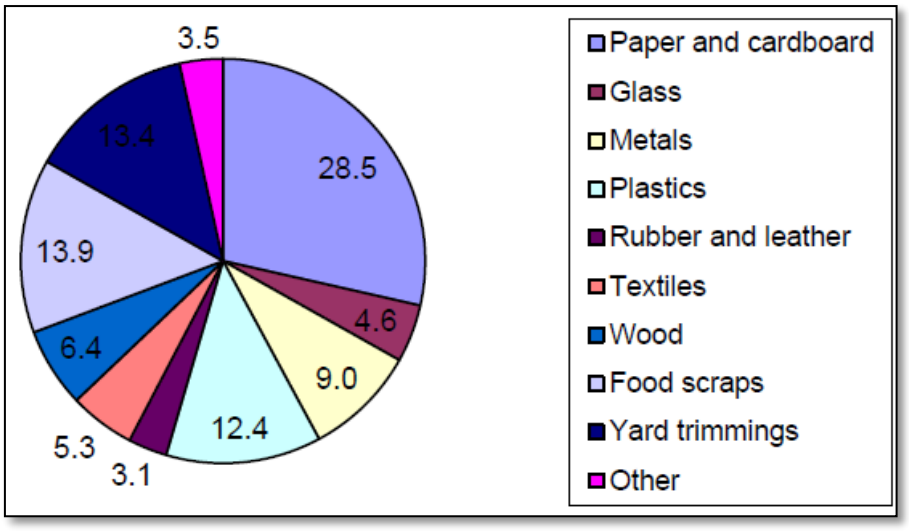


Figure 2-2: 2010 MSW waste materials (%) as generated in United States in 2010 (adapted from Mihelcic and Zimmerman, 2013).

b. Municipal solid waste composition in the developed and developing countries

The MSW components are similar throughout the world for the developed and developing countries (Mihelcic & Zimmerman, 2013). However, each country or region differs in the quantity of solid waste generated, the composition and density of the waste. The largest difference occurring in the MSW of developed and developing countries is the organic content in the solid waste produced (Diaz et al., 1996). According to Diaz et al. (1996) and Mihelcic and Zimmerman (2013) a large fraction of the waste produced by developing countries is organic, while developed countries produce less. This is because most of the developing countries are of low-income households that prepare food from the base ingredients. The developed countries, on the other hand, generate more inorganic material, which is mainly from packaging waste due to their high-income status. MSW composition for developing countries is presented in Table 2-3 while Table 2-4 present solid waste composition by percentages in developing countries.

Table 2-3: Composition of Solid Waste of Developing Countries. (Adapted from Mihelcic 2013)

Location	Food waste	Paper	Metals	Glass	Plastic, rubber, leather	Textiles	Ceramics, dust, ash, stones	Generation (Mg person^{-1} year^{-1})
Bangalore, India	75.2	1.5	0.1	0.2	0.9	3.1	19	0.146
Manila, Philippines	45.5	14.5	4.9	2.7	8.6	1.3	27.5	0.146
Asuncion, Paraguay	60.8	12.2	2.3	4.6	4.4	2.5	13.2	0.168
Mexico City, Mexico	59.8*	11.9	1.1	3.3	3.5	0.4	20	0.248
Bogota, Colombia	55.4*	18.3	1.6	4.6	16	3.8	0.3	0.27

* Includes small amounts of hay, straw and wood.

Note. Copyright 2013 by Mihelcic and Zimmerman. Reprinted by permission.

Table 2-4: Percentages Composition of Solid Waste in Developing and Developed Countries. (Adapted from Diaz et al., 2007).

	Low Income (%)	Middle Income (%)	High Income (%)
Organic	41.0	57.6	27.8
Paper	4.6	14.9	36.0
Plastic	3.8	10.9	9.4
Glass	2.1	2.4	6.7
Metal	1.0	3.1	7.7
Others	47.5	11.1	12.4

Note. Retrieved from Management of Solid wastes in developing countries book. Copyright 2007 by Diaz, Eggerth and Savage. Reprinted by permission.

2.3 Landfilling

As mentioned before, landfilling has become one of the most popular and preferred methods for managing MSW in both developed and developing because it is economical and applies to all components of the MSW (Shivayogimath & Watawati, 2013; Syafalni et al., 2012). Landfill can be defined as a land-engineered method of solid waste management that minimises environmental risks and nuisance (Qasim & Chiang, 1994). Figure 2-3 shows a cross-section of a typical modern landfill with its different engineered components that minimise public health and environmental risk. For this method to be effective in minimising public health and environment hazards, it requires an appropriate site selection, design, preparation and operation. The MSW is spread and compacted in thin layers (small practical volumes) and then covered with compacted earth or soil to limit exposure to water and air (Mihelcic & Zimmerman, 2013; Qasim & Chiang, 1994). Water that find its way into the compacted waste becomes a wastewater that is called leachate and is the main focus of this research.

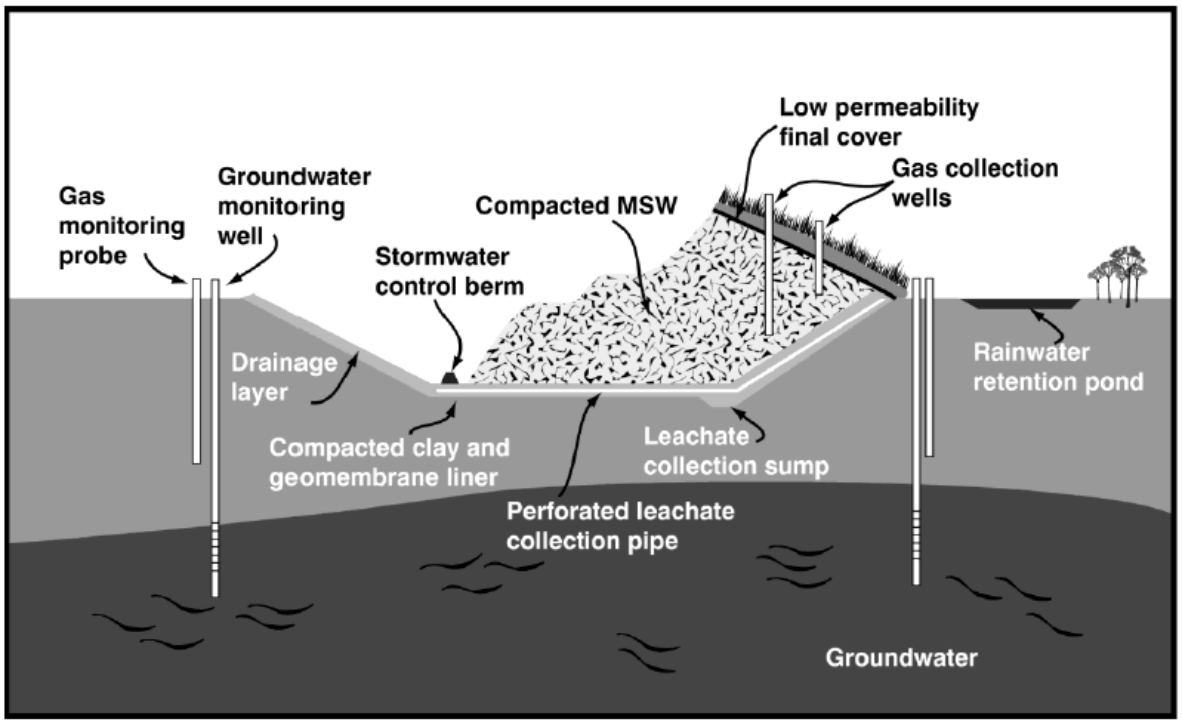


Figure 2-3: A typical modern landfill cross-section showing different engineered components (Mihelcic and Zimmerman 2013).

2.4 Leachate generation in landfill

Leachate production is a very important environmental concern and therefore the most important component of focus on this study. After being disposed of to a landfill, MSW undergoes various changes: physical, biological and chemical reactions (Mihelcic & Zimmerman, 2013; Qasim & Chiang, 1994). Water that finds its way into the compacted waste carries with it extractable chemicals and becomes a wastewater that is called leachate. The production of leachate in the landfill is a product of precipitation, infiltration, surface runoff, evaporation, storage capacity and biochemical processes. Figure 2-4 shows a schematic diagram of the water balance situation in a landfill environment. There are various factors that affect leachate generation, composition, stabilisation and the extraction of pollutants by percolating water (Bhalla, Saini, & Jha, 2012; Mihelcic & Zimmerman, 2013; Qasim & Chiang, 1994). These include the following:

1. characteristics of solid waste
2. availability of oxygen
3. landfill temperature
4. compaction rate
5. waste moisture content
6. amount of precipitation
7. landfill size and age
8. landfill pH
9. physical, biological chemical activities
10. hydrology of the site
11. geology of the site
12. climatic conditions

The amount of leachate generation can be determined by carrying out a water balance. The water balance equation (Equation 1) takes into account all the water entering and leaving the landfill (Diaz et al., 2007). This also includes water used in the biochemical processes, and water that evaporates through landfill gas (Diaz et al., 2007).

$$L = P - R - Du_s - ET - Du_w \quad \textbf{(1)}$$

where:

L = leachate production

P = precipitation

R = surface runoff

Du_s = change in soil moisture

ET = actual evaporation losses

Du_w = change in the moisture content of the solid waste components

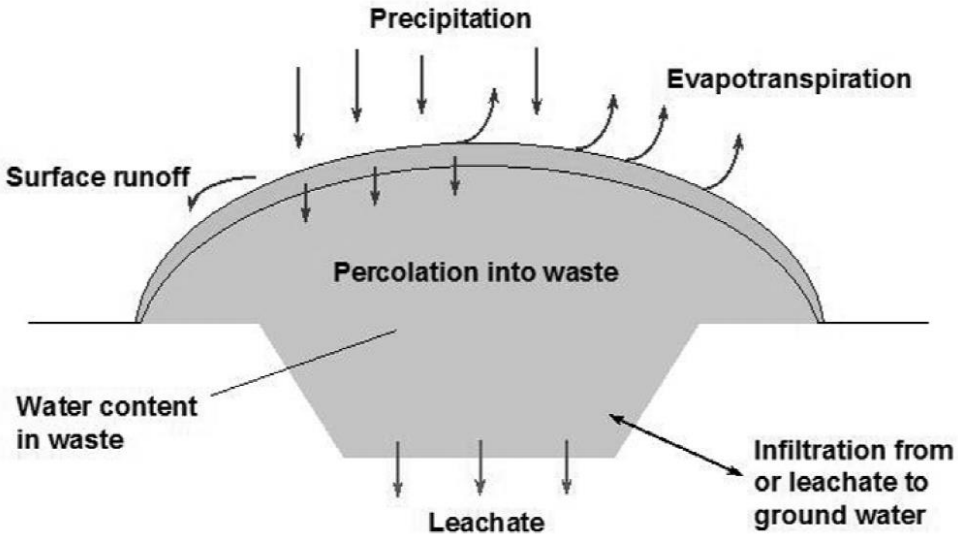


Figure 2-4: Leachate schematic diagram (Sami Serti, 2000).

2.5 Landfill leachate decomposition

As it ages, landfill undergoes a series of different stages. These stages rely on the physical, biological and chemical processes that take place in the landfill and they determine the production and composition of leachate (Bhalla et al., 2012; Mihelcic & Zimmerman, 2013; Qasim & Chiang, 1994). The leachate biodegradation goes through five phases that affect the composition of leachate, as shown in Figure 2-5 and Figure 2-6. These five phases are:

- Phase I – aerobic degradation
- Phase II – acid fermentation (anaerobic degradation)
- Phase III – methanogenic (anaerobic degradation)
- Phase IV and V – anaerobic degradation

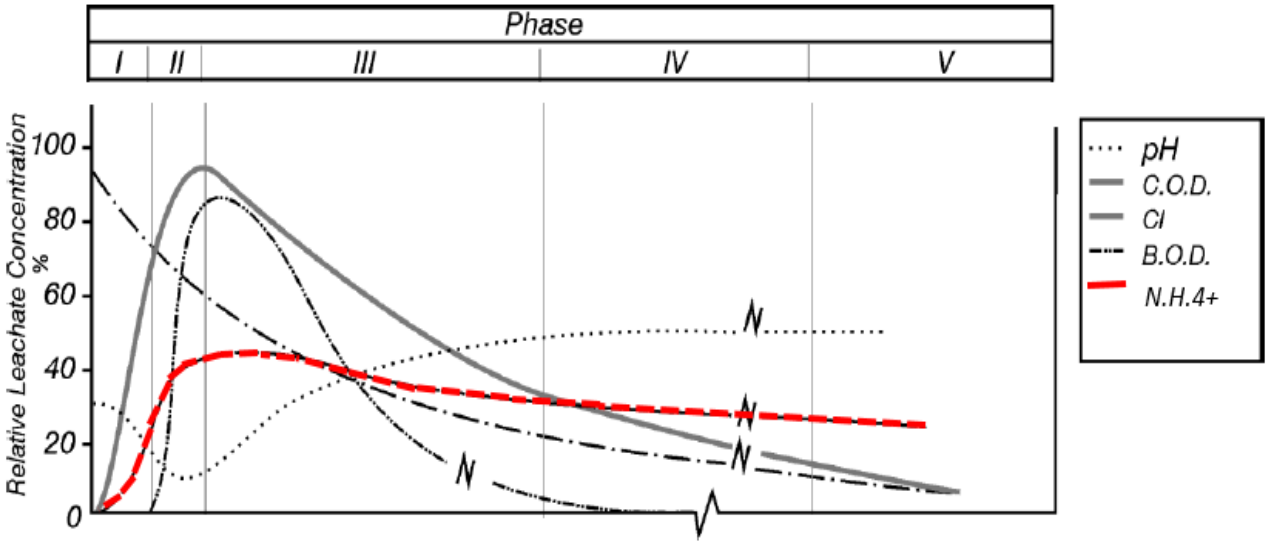


Figure 2-5: Landfill leachate chemical constituents over time (Johannessen, 1999).

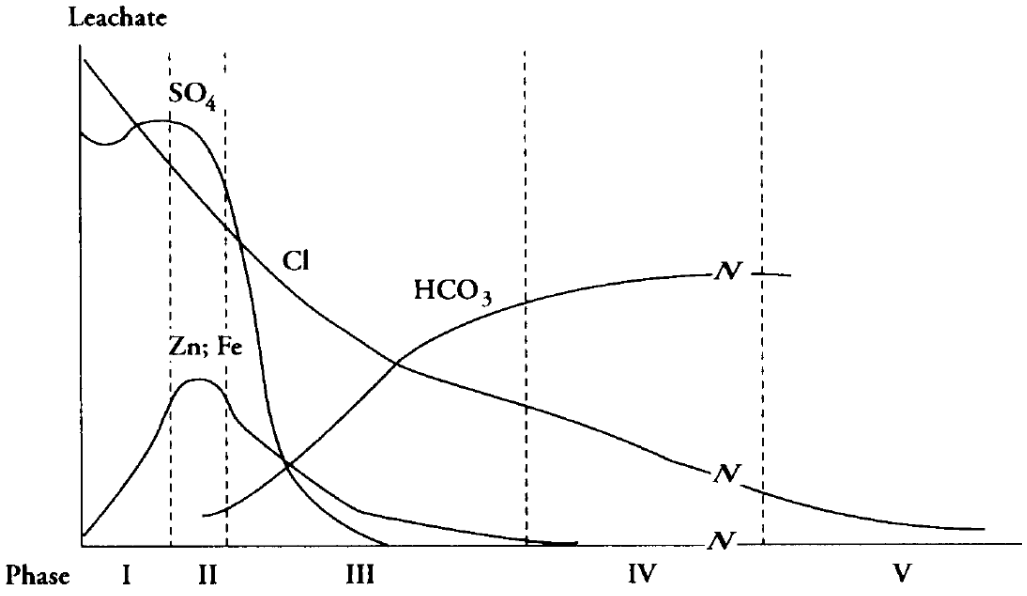


Figure 2-6: Landfill leachate chemical constituents over five phases (Johannessen, 1999).

2.6 Landfill leachate characteristics

Landfill leachates generally contain high levels of dissolved organic and inorganic matter with concentrations higher than those of groundwater (Christensen et al., 2001a). According to Christensen et al. (2001a), these concentrations could be higher by a factor between 1,000 and 5,000. The leachates vary both in volumetric flow and chemical composition. As mentioned before, the composition and concentration of the leachate depends on the type of the MSW deposited, the degree of solid waste stabilisation and the landfill age, among other factors (Guoa et al., 2010; Tsatsi et al., 2003). The leachate concentrations are said to change with time

as the landfill stabilises. The characterisation of landfill leachate is very important because it helps to identify the types of treatment possible. There are four groups of materials that characterise MSW leachate, as introduced by Peter Kjeldsen et al. (2002):

1. Organic matter: biodegradable and non-biodegradable expressed as COD, BOD5 or Total Organic Carbon (TOC). This also includes methane and volatile fatty acids.
2. Inorganic compounds: nitrogen (measured as ammonia and total nitrogen), magnesium, calcium, sodium, iron, potassium, manganese, sulfate, chloride and hydrogen carbonate.
3. Heavy metals (Zn, Ni, Pb, Cu, Cr, and Cd).
4. Xenobiotic organic compounds (XOCs): these include chlorinated aliphatics, phenols, and hydrocarbons. The source of XOCs are industrial chemicals, households, and according to Christensen et al. (2001b), they are in low concentration (< 1 mg/L).

Another way to characterise the landfill leachate is through the ratio of BOD5/COD. This indicates how biodegradable the organics are in leachate. Bashir et al. (2015) and de Velasquez, Monje-Ramirez, and Noguez (2012) used the BOD5/COD ratio to characterise the landfill leachate into three categories as follows:

- young leachates of not more than 5 years of age with BOD5/COD ratio ≥0.3 (acid phase and biodegradable)
- intermediate leachates from 5 to10 years with BOD5/COD ratio 0.1 to 0.3
- old or stabilised leachates of 15 years or more with a BOD5/COD ratio <0.1 (methanogenic-phase).

A typical MSW landfill leachate composition is presented in Appendix A. Moreover, Renou, Givaudan, Poulain, Dirassouyan, and Moulin (2008) captured and reported landfill leachate characteristics showing the age and levels of contaminants from landfill leachates of different countries, as shown in Appendix B. This kind of data is vital because it gives an idea of contaminant levels to be expected in the MSW leachate, and hence possible treatment methods required.

2.6.1 Organic content

As explained before, the organic content of leachate is used to characterise the landfill leachate in terms of its age and the degree of landfill stabilisation. This is through the ratio of BOD5/COD which indicates how biodegradable the organics are in leachate. According to Qasim and Chiang (1994) the ratio of BOD5/COD could increase to a high value of 19:20 hence influencing the type of leachate treatment employed.

2.6.2 Nutrients in leachate

The most abundant nutrient in most landfill leachates is nitrogen, as shown in Appendix A. The nitrogen concentration in the developed countries leachate can be found in the range from 600 to 5,000 mg total N/L (Johannessen, 1999). The organic nitrogen in the leachate undergoes anaerobic hydrolysis to form ammonia. According to Qasim and Chiang (1994) the ammonia concentration is present as the large proportions of total nitrogen in the acid phase of the landfill biodegradation stages. Moreover, in old landfills during methanogenic phases (phases III and IV) the ammonia nitrogen concentration levels makes about 85% to 95% of the total nitrogen content in the leachate (Qasim & Chiang, 1994).The other nutrient found in landfill leachate is phosphorus, which is often found in low concentration, as shown in Appendix A (Johannessen, 1999).

2.6.3 Heavy metals, chlorides and salts

Heavy metals are generally found in fairly low concentrations in landfill leachates (Christensen et al., 2001b). Kjeldsen and Christophersen (2000) conducted a survey on old Danish landfills and found the concentrations of heavy metals low. Their results were 0.07 mg/L of lead, 0.67 mg/L of zinc, 0.006 mg/L of cadmium, 0.13 mg/L of nickel, 0.08 mg/L of chromium and 0.07 mg/L of copper. More of their results are presented in Appendix C. Ahmadian et al. (2013), however, investigated the concentrations of heavy metals at different landfill stages and found that heavy metals have higher concentrations in earlier landfill stages. They explained that this could be because at low pH (phase II), the metals are highly soluble, hence high concentrations are detected. They also reported very low concentrations of heavy metals at later landfill stages due to low metal solubility caused by increase in pH levels. Generally, landfill leachates are said to have high salt concentrations when compared to municipal wastewaters and this often causes problems to the receiving environment (Morling, 2007). Very high chloride concentrations tend to corrode the environment and also affect the wastewater treatment plant processes (Morling, 2007).

2.7 Nitrogen in landfills

Nitrogen is introduced to the landfill through proteins from organic waste: food wastes, yard wastes and biosolids waste (Christensen & Kjeldsen, 1995). According to Diaz et al. (1996) and Mamo, Molina, Rosen, and Halbach (1998), about 7.0 to 18 g/kg of nitrogen by dry weight is contained in the MSW. Moreover, according to Jokela, Kettunen, Sormunen, and Rintala (2002), proteins are the main source of nitrogen in landfill leachate and about 0.5% by dry mass of proteins is in MSW. These proteins are mainly from organic matter in the MSW generated by the residential areas, commercial and institutional sources. Table 2-5 presents contributors of nitrogen and other organics in the solid waste. Yard waste and food waste produce the highest nitrogen components (3.4% and 2.6% respectively).

Table 2-5: Composition of Nitrogen and Other Organics (Mihelcic & Zimmerman, 2013).

	Moisture (% by wet mass)	**Energy value as received** (MJ/kg)	**Energy value after drying** (MJ/ kg)	**Carbon (% by dry mass)**	**Hydrogen (% by dry mass)**	**Oxygen (% by dry mass)**	**Nitrogen (% by dry mass)**
Food wastes	70.0	4.2	13.9	48.0	6.4	37.6	2.6
Magazines	4.1	12.2	12.7	32.9	5.0	38.6	0.1
Paper (mixed)	10.0	15.8	17.6	43.4	5.8	44.3	0.3
Plastics (mixed)	0.2	32.7	33.4	60.0	7.2	22.8	< 0.1
Textiles	10.0	18.5	20.5	48.0	6.4	40.0	2.2
Rubber	1.2	25.3	25.6	69.7	8.7	< 0.1	< 0.1
Leather	10.0	17.4	18.7	60.0	8.0	11.6	10
Yard wastes	60.0	6.0	15.1	46.0	6.0	38.0	3.4
Wood (mixed)	20.0	15.4	19.3	49.6	6.0	42.7	0.2
Glass	2.0	0.2	0.2	0.5	0.1	0.4	< 0.1
Metals	4.0	0.6	0.7	4.5	0.6	4.3	< 0.1

Note. Retrieved from Environmental Engineering book. Copyright 2013 by Mihelcic and Zimmerman.

2.8 Ammonia nitrogen pathway in landfill leachate

As mentioned earlier nitrogen is introduced to the landfill through proteins from organic waste (Christensen & Kjeldsen, 1995). The microorganisms in the solid waste hydrolyse and ferment the proteins producing ammonium nitrogen. This process is called ammonification (Berge & Reinhart, 2005). Hydrolysis and fermentation results in leachate with high ammonia nitrogen in old landfills (Berge & Reinhart, 2005; Peter Kjeldsen et al., 2002). Figure 2-7 shows potential nitrogen transformation pathways in the landfill environment. Previous studies have reported ammonia nitrogen concentrations in leachates ranging from levels below detection to

greater than 5,000 mg/L (Berge & Reinhart, 2005; Bhalla et al., 2012; Christensen et al., 2001b). Ammonification occurs in a two-step progression (Berge & Reinhart, 2005). Initially the proteins are hydrolysed either by aerobic or anaerobic bacteria producing amino acids. Secondly, the amino acids are fermented into ammonia nitrogen, volatile acids and CO_2 as shown in Figure 2-8 (Berge & Reinhart, 2005). During ammonification, ammonia is dissolved in the leachate and can undergo different transformations such as volatilisation, sorption, anammox, denitrification, nitrification and others (Berge & Reinhart, 2005). As ammonification takes place, the pH can vary, resulting in either ammonia or ammonium.

Ammonium nitrogen in water/leachate exists in two forms: NH_3 (free ammonia) and NH_4^+ (ionised ammonium) as shown in Equations 2 and 3. The balance of the equilibrium depends on pH and temperature.

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \ldots\ldots\ldots\ldots \quad \textbf{(2)}$$

$$NH_3 + H_3O \leftrightarrow NH_4^+ + H_2O \ldots\ldots\ldots\ldots \quad \textbf{(3)}$$

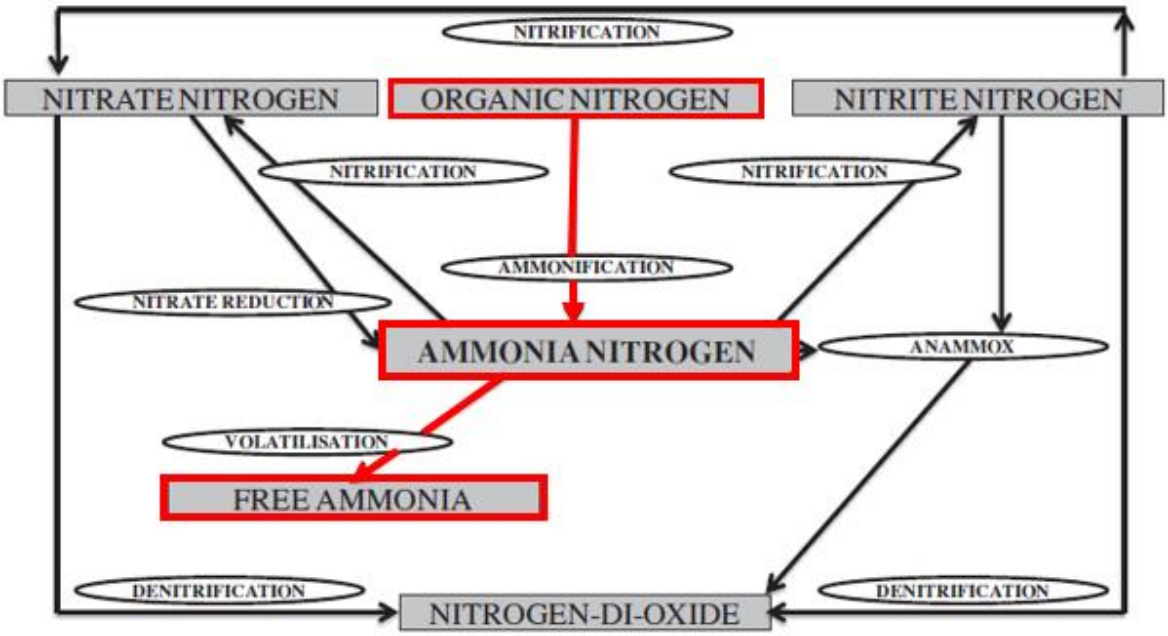


Figure 2-7: Potential nitrogen transformation pathways that may commonly occur in landfill. (Berge & Reinhart, 2005)

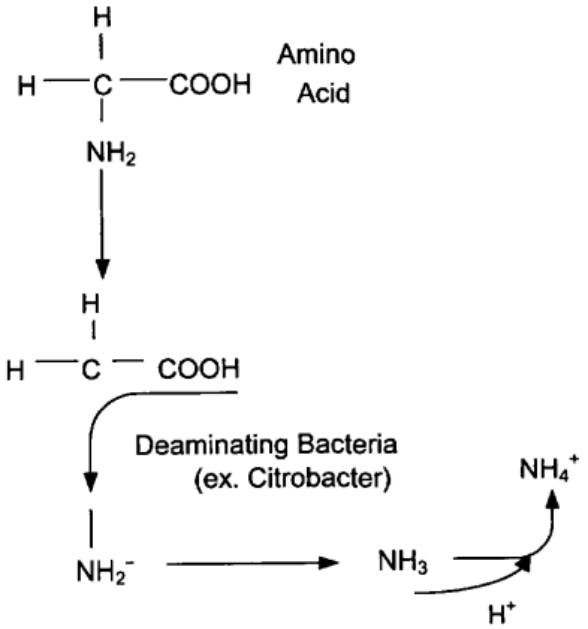


Figure 2-8: Ammonification process (Berge & Reinhart, 2005).

2.8.1 Problems caused by nitrogen and ammonia nitrogen

Nitrogen is a nutrient that is needed by plants for growth. However, excess nitrogen promotes algal bloom, hence contributing to eutrophication in the surrounding water bodies (Berge & Reinhart, 2005; Johannessen, 1999; van Loosdrecht, Nielsen, Lopez-Vazquez, & Brdjanovic, 2016). Concentrations of ammonia nitrogen higher than 500 mg/L impact negatively on degradation processes such as the biological nitrification process in the wastewater treatment plant (Berge & Reinhart, 2005). This results in reduced quality of the effluents, which do not then meet with the discharge standards. However, the anaerobic process benefits from concentrations ranging between 50 mg/L to 200 mg/L in wastewater treatment. Berge and Reinhart (2005) reported that concentrations of ammonia ranging between 200 mg/L and 1,000 mg/L have adverse effects on wastewater degradation processes. Moreover, other reports indicate that most of the effect on wastewater degradation processes is due to ammonia nitrogen concentrations ranging from 1,500 mg/L to 5,500 mg/L. Concentrations of ammonia above 5,800 mg/L create a very toxic environment to some microorganisms in the wastewater process (Berge & Reinhart, 2005).

At high pH, above pH 6.5, ammonia is increasingly in the form NH_3 and is very toxic to aquatic life (Berge & Reinhart, 2005). However, at pH values below pH 6.5 ammonia is almost all in

the form NH_4^+ and does not cause any adverse effect to aquatic life. However too low pH results in an acidic environment, also toxic to aquatic life.

Ammonia plays a major role in biological oxygen demand (BOD) addition into receiving waters (Jorgensen, 2002; Mihelcic & Zimmerman, 2013). The process of ammonia conversion to nitrates through nitrification demands large quantities of dissolved oxygen. This high oxygen demand causes dissolved oxygen depletion from receiving water bodies. For example, the equation below shows oxidation of NH_4^+ into nitrates where two moles of O_2 are consumed for every mole of ammonia nitrogen oxidised.

$$NH_4^+ + 2O_2 \leftrightarrow NO_3^- + 2H^+ + H_2O \quad \textbf{(4)}$$

Most importantly, landfill leachate with high ammonia concentration has proven too challenging and too expensive for municipalities to manage especially during biological treatment in wastewater treatment plants. Because of this, the Christchurch City Council (CCC) treatment plant charges fees based on ammonia concentrations, as well as BOD, COD, volume and heavy metal concentrations, thus prompting this research.

2.9 Ammonia treatment Methods from landfill leachate

Landfill leachate treatment is required before discharging it to the environment. Treatment is probably needed to remove ammonia nitrogen, organic matter, trace metals, and xenobiotic organics. The treatment is beneficial to wastewater treatments plants for the effective operation of biological treatment (Poveda et al., 2016; Rui et al., 2012). In some areas, sewage treatment plants refuse to treat landfill leachate because the leachate may contain high concentrations of inhibitory chemicals that might interfere with the facility treatment process (Mulamoottil et al, 1999).

Treatment methods of landfill leachate are influenced by the specific composition and concentration of ammonia and COD. According to studies by Guoa et al. (2010) and Marañón, Castrillón, Fernández-Nava, Fernández-Méndez, and Fernández-Sánchez (2008a), biological treatments such as aerobic activated sludge and anaerobic digestion are the most popular. This is because they are relatively effective in treating younger leachates with a high BOD5/COD ratio. However, most of the treatment methods are usually limited by operational cost, complexity, and regulations by the authorities (Rui et al., 2012). According to Tsatsi et al.

(2003) the most ideal and common technologies for leachate treatment use the physico-chemical method. Tsatsi et al. (2003) further regard the physico-chemical method as effective in treating leachate and also simple in operation, low in capital and with reduced operational costs.

There are a number of effective physico-chemical technologies that can be used as pretreatment methods for landfill leachates, and focus on ammonia with processes such as air stripping, ion exchange, precipitation, adsorption and coagulation–flocculation. Some of the physico-chemical methods are discussed below.

2.9.1 Physico-chemical methods

2.9.1.1 Air stripping

This method is used in pretreatment of wastewater and landfill leachate to remove high concentrations of ammonia and other volatile compounds such as volatile organic compounds (Metcalf & Eddy, 1991; Qasim & Chiang, 1994). As shown in Figure 2-9, air or gas is blown from the bottom of the stripping tower while liquid or water is injected to the top of the tower and flows down through the packing. Ammonium hydroxide will then be formed as ammonia or VOCs are stripped out of the leachate into air. Equation 5 below show the conversion of ammonium into ammonia gas taking place in the stripping tower.

$$NH_4^+(aq) + OH^- \rightarrow NH_3(g) + H_2O \quad \textbf{(5)}$$

The efficiency of this pretreatment method depends on temperature, pH, rate of air supply, gas transfer rate and hydraulic loading rate (Metcalf & Eddy, 1991; Qasim & Chiang, 1994). Air stripping generally achieves up to 90% of ammonia and VOCs removal (Metcalf & Eddy, 1991; Qasim & Chiang, 1994). However, this method releases VOCs into the atmosphere, which is always of concern for the environment. Moreover, another major problem caused by this method is calcium carbonate scaling. This study did not consider air stripping as an option for the removal of landfill leachate ammonia.

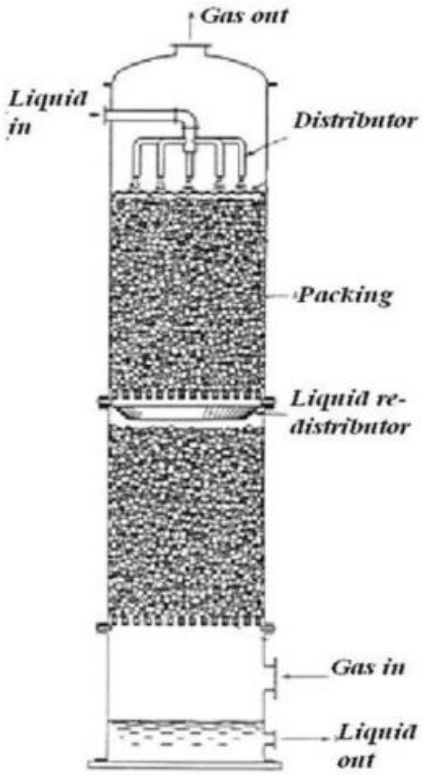


Figure 2-9: Air stripping tower set-up (Qasim & Chiang, 1994).

2.9.1.2 Ion exchange

Ion exchange is a physico-chemical method used to remove toxic ions (e.g. ammonium loads) and heavy metals from dilute solutions using the principle of adsorption. This method involves the exchange of ions between an aqueous solution and a solid substance known as a resin bed or ion exchanger (Prajapati, Syed, & Chauhan, 2014; Qasim & Chiang, 1994). Zeolite and synthetic resins (silica powder) are the most common types of resins used for the removal of ammonium ion from wastewater (Prajapati et al., 2014). The effectiveness of zeolites in the removal of ammonium ion depends on the presence of other cations (Wang et al., 2006).

Equation 6 shows the affinity potential of other cations in comparison to NH_4^+ and some of these cations affects the removal of ammonium ions if present in landfill leachate or wastewater.

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} \quad \textbf{(6)}$$

Equation 7 illustrates the equilibrium phase in ion exchange and Figure 2-10 shows when ions from resin meet ions from wastewater/leachate. A schematic diagram showing ammonia removal from wastewater using zeolites is shown in Figure 2-11.

$$A_r^+ + B_{aq}^+ \leftrightarrow A_{aq}^+ + B_r^+ \ldots\ldots\ldots\ldots \quad \textbf{(7)}$$

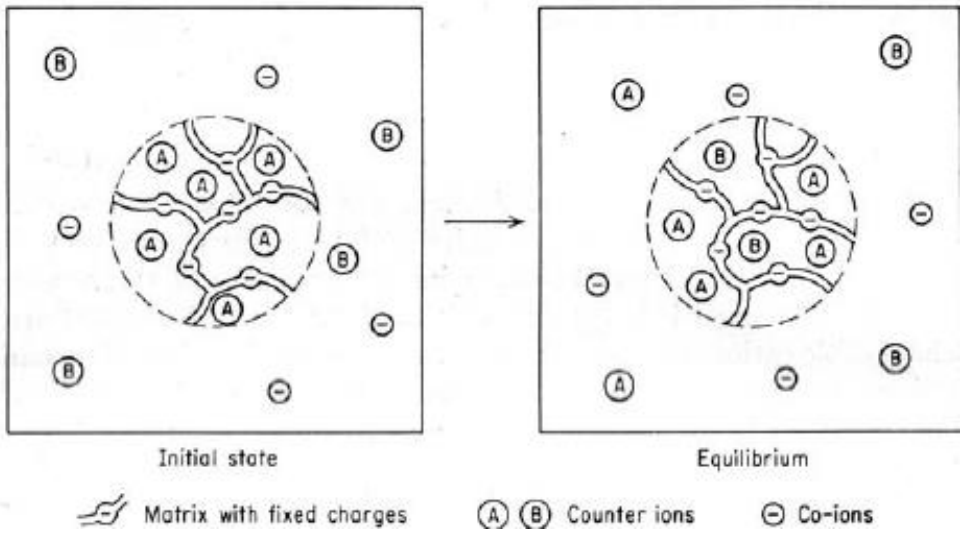


Figure 2-10: Equilibrium phase in ion exchange

However, a disadvantage of this method is the production of hardness which needs further treatment (Qasim & Chiang, 1994). This can be achieved by application of a primary softener to break down the hardness, followed by a polisher for the ammonia, which can be costly (Qasim & Chiang, 1994). Another problem with this method is fouling. This makes this method generally unsuitable as a pretreatment method for this study.

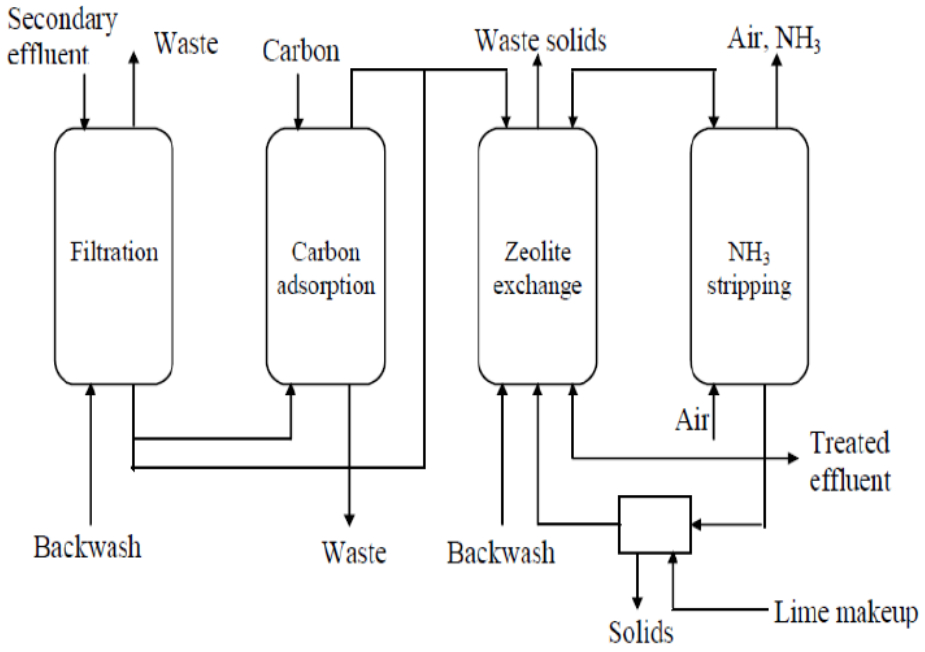


Figure 2-11: Schematic diagram showing ammonia removal from wastewater using zeolites (Jignasha et al. 2014)

2.9.1.3 Coagulation–flocculation

a. Introduction

Coagulation–flocculation has become a popular treatment method for landfill leachate as it is less sensitive to fouling than other methods (Aziz, Adlan, Zahari, & Alias, 2004). Moreover, coagulation–flocculation has proven to be an effective treatment method for reducing COD, colour, heavy metals, and suspended solids, with 60% to 90% removal achievable with many leachates (Bashir et al., 2015; Syafalni et al., 2012). More results of these studies are presented in Appendix D.

b. Coagulation

Coagulation is a simple method commonly used to remove colloidal matter of suspended solids (SS), non-biodegradable organic compounds and heavy metals from landfill leachate and wastewater (A. Amokrane, C. Comel, & J. Veroni, 1997; Marañón, Castrillón, Fernández-Nava, Fernández-Méndez, & Fernández-Sánchez, 2008b; Poveda et al., 2016). The method involves adding coagulant to wastewater or leachate, which destabilises colloidal particles of around 0.01 to 10 μm. Some common coagulants used in water and wastewater treatment include metal salts such as ferric chloride, polyaluminum chloride (PAC), ferric sulfate, aluminium sulfate (alum), ferrous sulfate, lime etc. As the coagulant is added the electrical

charges that maintain colloids in suspension in the leachate are neutralised. Rapid mixing is also employed to facilitate particle collision hence increasing their size. Studies by Aziz et al. (2007) and Al-Malack (1999) explain that the degrees of destabilisation in coagulation–flocculation depends on coagulants used.

c. Colloids

Coagulation and flocculation depend on the interaction of colloids (Kang, 1994). The very important characteristics of colloids is their small volume and a large surface area, which are key to the coagulation–flocculation process (Kang, 1994). The colloids are of two types – hydrophilic and hydrophobic. Hydrophilic colloids are unstable, and destabilises easily (Kang, 1994). These include clay and nonhydrated metal oxides. Conversely, hydrophobic solids are stable and form colloidal solutions that are not easily destabilised when mixed with water. An example of these is soap (Koohestanian, Hosseini, & Abbasian, 2008). The colloidal particle stability is indicated by zeta potential (Zp) magnitude. The zeta potential is the charge of the colloid (Yu, 1999). A high Zp indicates a very stable colloid in suspension due to much greater repulsive forces between the particles, whereas unstable colloids are indicated by a lower Zp where particles do aggregate (Koohestanian et al., 2008). Moreover, Zp is a very useful character to control the coagulation process. The Zp changes in colloids hence influencing the repulsive force between particles.

As shown in Figure 2-12, the surface potential of colloids is also an important characteristic of coagulation and flocculation. The concentration of ions in the solution influences the relationship between surface potential and zeta potential. Figure 2-12(a) shows a preferred relationship between Zp and surface potential due to a larger double layer in fresh water. While in saline water, the relationship is not that preferred due to a compressed double layer, as shown in Figure 2-12(b). Colloids particles are stable in wastewater because of their surface charge, and to destabilise them a coagulant such as a metallic salt is needed to remove these hydrophilic colloids. Hence this study investigated ferric chloride and alum as coagulants to destabilise the colloids in landfill leachate.

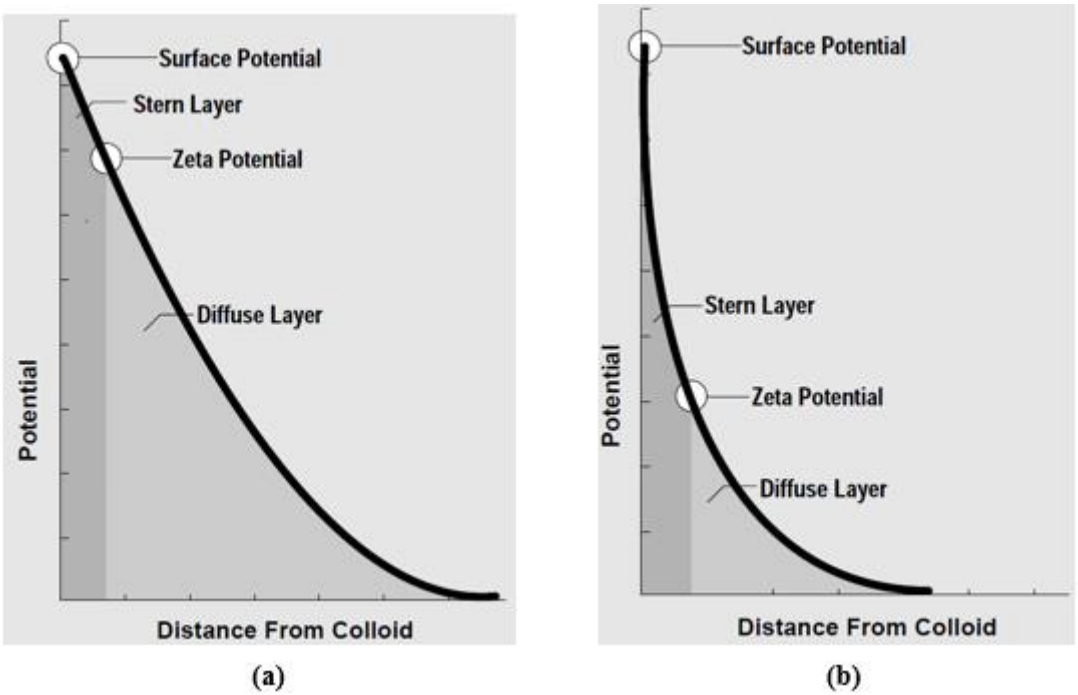


Figure 2-12: Zeta potential in (a) fresh water and saline water (b). (Adapted from Koohestanian et al., 2008).

d. Effect of particles size and charge on coagulation (electrokinetic connection).

The ability of a coagulant to coagulate depends on its particle size and charge (Kang, 1994). Colloids of particle size ranging from 0.01–10 μm easily settle during coagulation. However, colloids of smaller size (lower than 0.01 μm) present difficulties in settling, and hence affect the coagulation process (Koohestanian et al., 2008; Ravina, 1993; Yu, 1999). Figure 2-13 shows typical sizes of the various particles in water requiring treatment. The smaller particles tend to settle slowly, and hence are likely to be sampled with the decanting liquid. Moreover, the behaviour of colloid particles in solution are influenced by their electrokinetic charge (Koohestanian et al., 2008; Ravina, 1993; Yu, 1999). Colloid particles carry a negative charge and a group of them with like charges in a solution repel each other, preventing agglomeration (Figure 2-14). As the charge is reduced or removed, however, the particles will bond together by forming small groups and increase into visible floc particles that will settle, as illustrated in Figure 2-15 (Ravina, 1993).

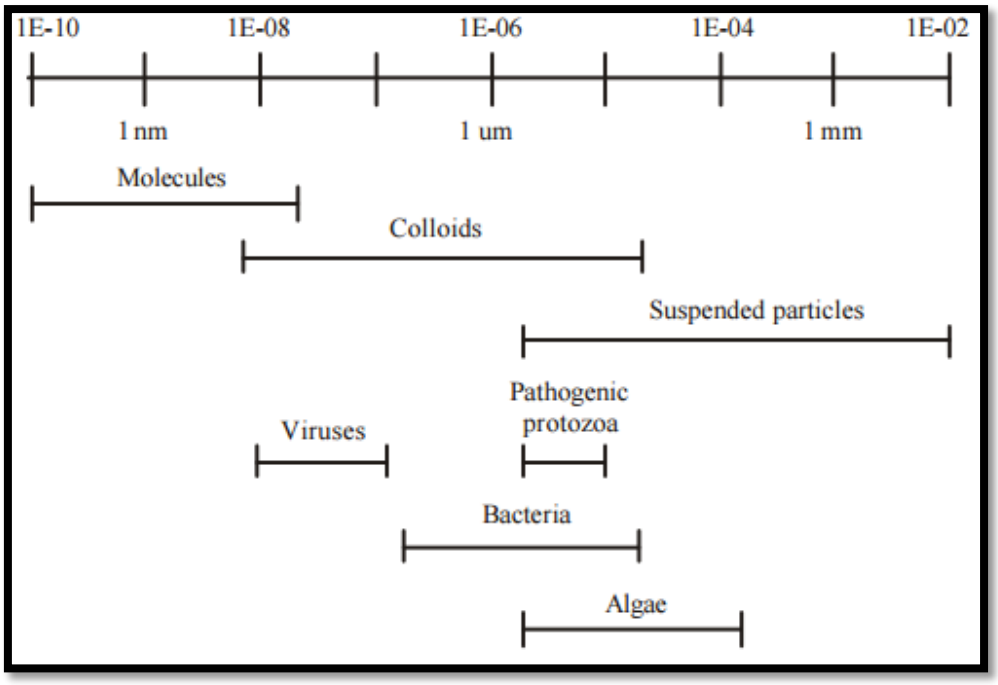


Figure 2-13: Possible particle sizes in water treatment. (Adapted from Koohestanian et al., 2008)

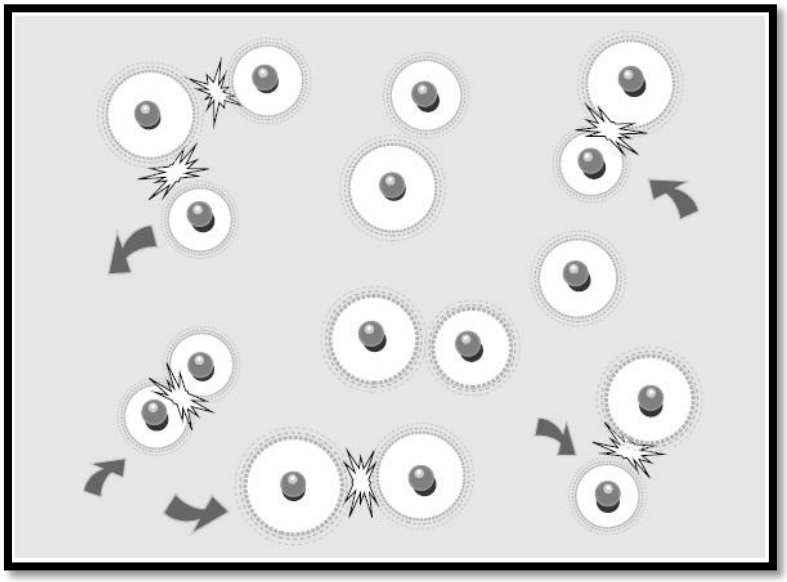


Figure 2-14: Like-charged particles in solution repelling each other. (Adapted from Ravina, 1993).

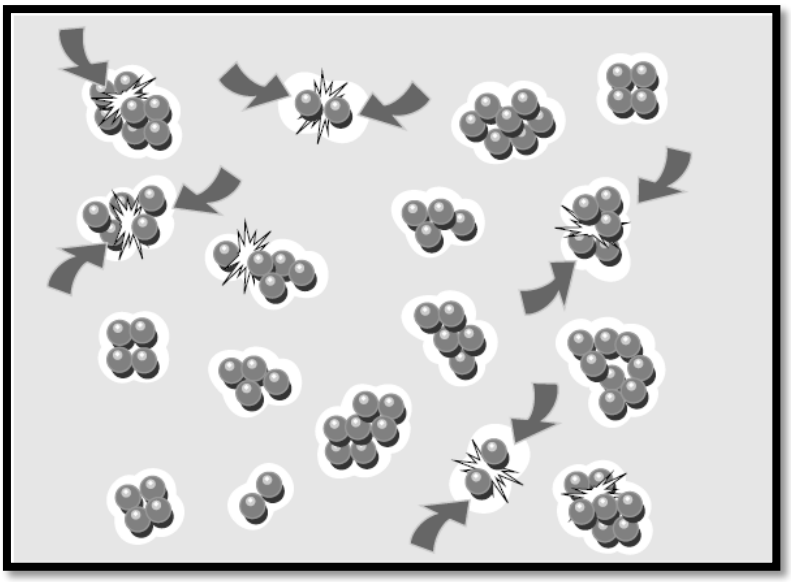


Figure 2-15: Uncharged particles colliding. (Adapted from Ravina, 1993)

e. Double layer model

To illustrate how electrical attraction and repulsion occurs between charged particles in an ionic environment as shown in Figure 2-14 and Figure 2-15, a double layer model can be used. For example, if there are counter-ions (positive ions) in a solution, the negative particles will attract the counter-ions to attach themselves around the particle surface and form a stern layer as shown in Figure 2-16. As more positive ions approach the negative colloid they will now be repelled by the stern layer around the negative colloid particle and other nearby positive ions, resulting in an equilibrium state (Koohestanian et al., 2008; Ravina, 1993; Yu, 1999).

Equilibrium state is the result of a concentration of positive ions in the solution due to repulsion forces. As the concentration of positive ions increase around the particle, they reach equilibrium. Likewise, if there are co-ions (negative ions) in the solution they will be repelled by a negative colloid particle, hence increasing their concentration. This will also result in them reaching equilibrium (Koohestanian et al., 2008; Ravina, 1993; Yu, 1999).

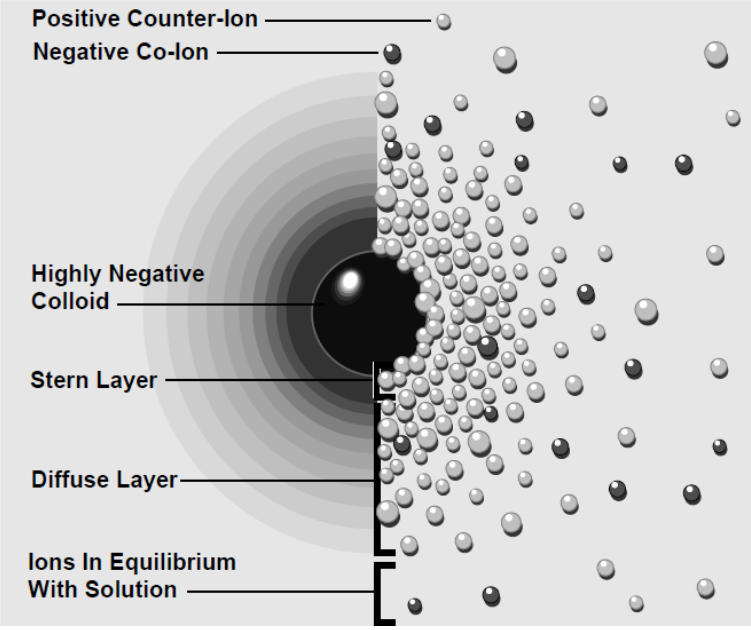


Figure 2-16: Double layer illustration model. (Adapted from Ravina, 1993)

f. Coagulation tools – destabilisation process

Coagulation and flocculation are known to be caused by either double layer compression, charge neutralisation, bridging or colloid entrapment (Ravina, 1993; Yu, 1999). Double layer compression involves dosing the wastewater with a coagulant (metal salt) resulting in a metal hydroxide precipitation (Ravina, 1993; Yu, 1999). Precipitation is key in the coagulation process, because it is a way of converting soluble substances into solid form. If coagulants (ferric chloride and alum) are used, then the metal hydroxide precipitates will be $Fe(OH)_3$ and $Al(OH)_3$ respectively. These precipitates will settle and carry colloidal particles down with them.

During the charge neutralisation, positively charged coagulants in the wastewater will be adsorbed on the surface of the colloid. The negative charge from the colloidal contained in the wastewater and the positive charged coagulants will neutralise, yielding a net zero charge. Neutralisation is very important in optimising treatment and facilitates the settling of particles (Ravina, 1993; Yu, 1999). However, neutralisation does not form flocs visible to the naked eye. To monitor and control the charge neutralisation, a zeta potential measurement can be used, as mentioned earlier. The zeta potential measurement is important to control effects such as overdosing, which can affect the charge of the colloid and the van der Waals attraction, so yielding poor flocculation (Ravina, 1993).

The last process that takes place in coagulation is bridging. It occurs when a thread or fibres from a coagulant are attached to numerous colloids in wastewater, binding them together, as shown in Figure 2-17 (Ravina, 1993; Yu, 1999). Together they are called a floc, which is the next process discussed under flocculation. Normally this takes place when the surface charge is almost zero (charge neutralisation). The effectiveness of bridging depends on the molecular weights of coagulants (Ravina, 1993; Yu, 1999). The higher the molecular weight, the longer the molecules, and hence highly effective bridging occurs.

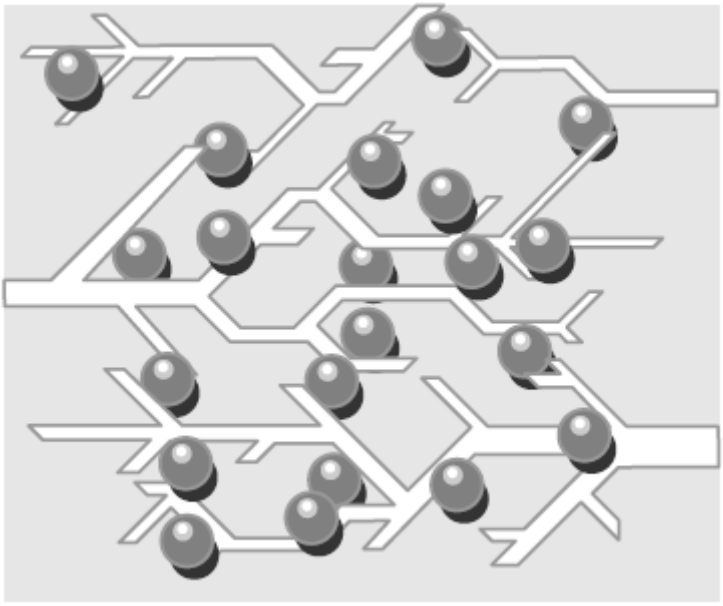


Figure 2-17: Coagulant fibres attached to numerous colloids (Adapted from Ravina, 1993)

g. Flocculation

Following coagulation is a second process called flocculation. When particles have been destabilised due to the coagulation process, they collide and come together under hydraulic shear forces (Karadag et al., 2008). This results in agglomeration of colloid particles and bridging to form microflocs. With the slow mixing that takes place in the flocculation process, the microflocs increase in size to form visible masses of flocs called pinflocs. As more collisions take place due to the interaction with inorganic polymers from the coagulant or with the addition of organic polymers, more pinflocs continue to build. This results in formation of macroflocs (Karadag et al., 2008). With the addition of high-molecular-weight polymers, processes such as bridging, binding of molecules and floc strengthening are facilitated. These cause floc to reach their optimum strength and size (gain weight), resulting in settling. Flocculation diagram is shown in Figure 2-18.

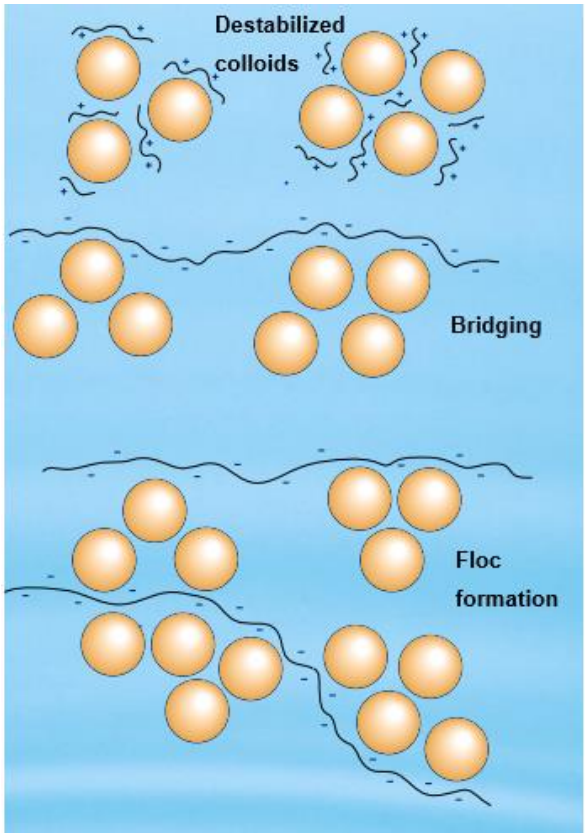


Figure 2-18: Schematic of the flocculation process. (Karadag et al., 2008)

Flocculation has two stages: perikinetic flocculation and orthokinetic flocculation (Bratby, 1980). The first, perikinetic flocculation stage, also known as Brownian movement (thermal agitation), begins immediately after the destabilisation process. This stage normally happens just for a few seconds since after this the floc sizes are greater than the Brownian motion range therefore, can be little or not affected (Bratby, 1980). Brownian motion is key for collisions of particles smaller than 0.1 μm provided there is complete destabilisation of particles, and also the particles are not too large and so outside the Brownian motion range (Bratby, 1980).

The second stage, orthokinetic flocculation, is caused by induced velocity gradients in the fluid due to mixing (Bratby, 1980). Induced velocity gradients are introduced by setting the fluid in motion and this could be by mechanical agitation within a flocculation reactor. The velocity gradients are important because they provide opportunity for contact between particles, hence, cause settling. The rapid settling of particles by gravitational force in this stage also cause particles that are smaller and with slower settling velocities to be carried along. Orthokinetic flocculation is key for collision of particles greater than 1.0 μm (Bratby, 1980).

h. Coagulants

As mentioned before, coagulants are needed to destabilise the surface charge of the wastewater stable colloid particles (hydrophilic colloids) in landfill leachate and possibly remove ammonia nitrogen. The two common types of coagulants used are mineral (inorganic) coagulants and organic coagulants. The mineral coagulants are mainly metal salts and those commonly used are based on iron and aluminium (Bratby, 1980). They include but are not limited to the following:

- ferric chloride ($FeCl_3$)
- ferric sulfate ($(Fe_2(SO_4)_3.8H_2O$)
- ferrous sulfate ($FeSO_4.\ 7H_2O$)
- alum ($Al_2(SO_4)_{3.}4H_2O$)
- aluminium chloride ($AlCl_3.\ 6H_2O$)
- sodium aluminate ($NaAlO_2$)
- Polyaluminium chloride PAC
- Lime $Ca(OH)_2$

According to most studies, aluminum sulfate is the most efficient and commonly used coagulant in potable water while iron salts are the most efficient and commonly used in treating wastewaters. Different research papers, such as of Amokrane et al. (1997), Poveda et al. (2016), Tsatsi et al. (2003) and Renou et al. (2008) have demonstrated that iron salts are better coagulants than aluminium salts in treating wastewater and leachate. Their studies produced better removal of colour, COD, turbidity and suspended solids with ferric chloride than with alum. Appendix D provides an overview of studies that have examined the removal of COD, colour, turbidity and suspended solids from landfill leachate using coagulation–flocculation. Moreover, according to some studies, ferric chloride has also been increasingly and efficiently used in treating potable water. The mineral (inorganic) coagulants are highly charged and when added to water or wastewater they neutralise the colloidal particles. The metal salts listed above possess a cationic charge brought by the metallic ions (Fe^{3+} or Al^{3+}). These metallic ions when added to water or wastewater will result in the formation of iron hydroxides or aluminium hydroxides. These inorganic hydroxides produce short polymer chains that enhance the formation of microfloc (Kang, 1994). The cations' multivalent characteristics and insolubility strongly attract them to charged colloid particles in water and wastewater, resulting in contaminant removal. Most inorganic coagulants are widely available, low in price and, most

importantly, they are effective in the removal of a wide range of contaminants in water and wastewater. Moreover, during the coagulation process, as the large volumes of floc produced by inorganic coagulants settle, they are likely to trap some bacteria with them. In view of this, it is necessary to dispose of the settled flocs in an environmentally suitable way. Typical stoichiometric coagulation reactions are shown below in Equations 8 to11:

Ferric Chloride

$$2\,FeCl_3 + 3\,Ca(HCO_3)_2 \longrightarrow 2\,Fe(OH)_3 + 3CaCl_2 + 6CO_2 \quad \textbf{(8)}$$

Ferric Chloride + Calcium Bicarbonate (present in the water to treat) gives Ferric Hydroxide + Calcium Chloride + Carbon Dioxide

Ferric Sulfate

$$Fe_2(SO_4)_3 + 3\,Ca(HCO_3)_2 \longrightarrow 2\,Fe(OH)_3 + 3CaSO_4 + 6\,CO_2 \quad \textbf{(9)}$$

Ferric Sulfate + Calcium Bicarbonate (present in the water to treat) gives Ferric Hydroxide + Calcium Sulfate + Carbon Dioxide

Alum

$$Al_2(SO_4)_3 + 3\,Ca(HCO_3)_2 \longrightarrow 2\,Al(OH)_3 + 3CaSO_4 + 6\,CO_2 \quad \textbf{(10)}$$

Aluminum Sulfate + Calcium Bicarbonate (present in the water to treat) gives Aluminum Hydroxide + Calcium Sulfate + Carbon Dioxide

Ferrous Sulfate

$$FeSO_4 + Ca(HCO_3)_2 \longrightarrow Fe(OH)_2 + CaSO4 + 2CO_2 \quad \textbf{(11)}$$

Ferrous Sulfate + Calcium Bicarbonate (present in the water to treat) gives Ferrous Hydroxide + Calcium Sulfate + Carbon Dioxide

Table 2-6 present some of the inorganic coagulants used in the treatment of wastewater including their molecular weights and form. This study chose to investigate ferric chloride and alum metal coagulants because of the following characteristics:

- commonly used
- availability

- low cost
- capacity to produce multi-charged polynuclear structures in solution with enhanced adsorption characteristics.

Organic coagulants are characterised by long-chained and high-molecular-weight molecules (Bratby, 1980). There are four main groups or families of organic coagulant: polyDADMAC, polyamines, melamine-formaldehyde resins and dicyandiamide resins (Kay-Shoemake, Watwood, Lentz, & Sojka, 1998). PolyDADMAC and polyamines are the most used families of organic coagulants and function only by charge neutralisation. They are very effective in treating raw water with high turbidity (>20 NTU) and wastewater. Melamine-formaldehyde resins and dicyandiamide resins function by sweep floc mechanisms similar to most of the inorganic coagulants and are very effective in adsorption of organic (oil and grease) materials (Kang, 1994). However, they are very expensive to use as a coagulant. Organic coagulants are usually added in low dosages in coagulation, and often produce low volumes of sludge.

Table 2-6: Common Inorganic Coagulants Used in Wastewater Treatment. (Adapted from Metcalf and Eddy 1991).

Chemical	Formula	Molecular weight	Equivalent weight	Form
Alum	$Al_2(SO_4)_3 \cdot 18H_2O$	666.5		Liquid
	$Al_2(SO_4)_3 \cdot 14H_2O$	594.4	114	
Aluminum chloride	$AlCl_3$	133.3	44	Liquid
Calcium hydroxide (lime)	$Ca(OH)_2$	56.1 (as CaO)	40	Lump powder slurry
Ferric chloride	$FeCl_3$	162.2	91	Liquid lump
Sodium aluminate	$Na_2Al_2O_4$	163.9	100	Flake

i. Polyelectrolytes (Coagulant aids)

This study also investigated the use of some polyelectrolytes in trying to facilitate floc formation and optimise ammonia nitrogen removal. Polyelectrolytes or polymers play a different role from metal salts (Bratby, 1980). Polymers serve as aids to coagulants; polyelectrolytes, however, have the ability to destabilise colloids in water or wastewater but their primary role is to enhance flocculation by aiding coagulants (Bratby, 1980). Polyelectrolytes are either synthetic or natural, and consist of series of repeating chemical units (long chain organic molecules) held together by covalent bonds. These chemical units are either

homopolymer, copolymer or monomer. Homopolymer consist of repeating units of the same structure. Multirepeating chemical units refer to copolymers while monomers refers to individual repeating chemical units.

Polyelectrolytes have become popular in coagulation–flocculation processes, are known to be nontoxic, are used and effective in low dosages, and are easy to handle (Bratby, 1980; Yu, 1999). Their importance in the coagulation–flocculation process entails but is not limited to the following:

- reducing volumes of sludge generated by coagulation–flocculation
- aiding sludge digestion by microorganisms
- improving the sludge-dewatering process
- minimising chemical residuals in treated waters
- reducing the need for additional alkalinity for final pH control, and effective over a wide range of pH.

Polyelectrolytes are classified by molecular weight, form, charge or charge density (Bratby, 1980; Yu, 1999). The molecular weight of the polyelectrolytes refers to the sum of individual monomer's molecular weights. Polymer charge density (mole %) refers to the amount of electric charge concentration on a polymer chain. There is also the degree of polymerisation, which refers to the total number of monomer units. Anionic (negatively charged) polyelectrolytes are commonly used with metal coagulants. While cationic (positively charged) polyelectrolytes can be used as a coagulant, or with iron and aluminium based coagulants to attach to colloidal particles and for charge neutralisation. Categories of polymers are presented in Table 2-7.

Table 2-7: Categories of Polymers

Characteristics	Classification	
Molecular weight	Low	1 -3 millions
	Medium	3 – 6 millions
	Standard	6 – 10 millions
	High	10 – 15 millions
	Very high	> 15 millions
Charge	Cationic	+ve charged
	Anionic	-ve charged
	Non-ionic	no charge
Charge Density	Low	1–10%
	Medium	10–40%
	High	40–80%
	Very high	80–100%
Form	Aqueous	
	Liquid	
	Powder	
	Granular	
	Oil	

Note. Copyright 1980 by John Bratby.

The advantages of polymers are that they can be used at low doses, do not increase alkalinity, are toxic free, and produce lower volumes of sludge, as mentioned earlier (Bratby, 1980; Yu, 1999). Their disadvantage is that they can be very much more expensive than inorganic coagulants. For this study three cationic polyelectrolytes were investigated in ammonia nitrogen removal via coagulation–flocculation. These are Magnesol 598, Crystalfloc and Magnafloc LT 7991. These polyelectrolytes are discussed in detail in Chapter 4 of this study.

j. Factors affecting coagulation–flocculation

pH

During coagulation, the metal salt coagulants used dissociate in solution and release ions that are responsible for the coagulation process (Kang, 1994). These ions produced by the coagulant are vastly dependent on the pH of the sample (wastewater/leachate). The coagulation process can be affected by changing the sample (wastewater/leachate) pH values. This is likely to cause the formation of fewer of the necessary ions in the sample. For example, the coagulation process may not take place if the sample pH is too low, while higher pH values may result in

re-dispersion of coagulated particles (Kang, 1994). The size of flocs formed is also affected by pH, affecting its ability to settle or the settling rate. Most of the iron salts and aluminium salts are more effective at pH range 4.5 to 5.5 and 5.5 to 6.3 respectively. The sample pH values can be adjusted with alkalinity or acids. This study also investigated some of these pH values in optimising pollutant removal.

Temperature

Temperature also affects the efficiency of coagulation–flocculation. Low temperature are said to affect the mechanism of flocculation in water treatment plants, so decreasing the removal efficiency of turbidity in water treatment plants (Kang, 1994). Kang (1994) highlighted that varying the sample temperature could possibly affect the coagulation–flocculation kinetics. Examples given by Kang (1994) that could be affected by varying the sample temperature include the following:

1. The sample density and viscosity could be affected, hence reducing the strength of the colloidal matter. Colloidal matter requires strength during the coagulation stage for collision and transport.
2. Varying the sample temperature could possibly change the surface charges of the colloidal matter, hence tamper with charge neutralisation.
3. The rate and distribution of hydrolysis species of metal coagulant could also be affected.
4. The product (hydrolysis species) ion could also be changed by varying the sample temperature, hence changing the solution's pH.

2.9.1.4 Adsorption

Adsorption involves adsorbents with high internal surface area binding themselves with molecules in aqueous solution. An adsorbent refers to the solid constituent that provides the surface for adsorption, whereas adsorbate refers to the species being adsorbed (Worch, 2012). Figure 2-19 shows the basic terms used in adsorption theory. Adsorbents used for wastewater treatment may be of natural origin or industrially produced (engineered adsorbents). Typical adsorbents of natural origin that have been used in the removal of contaminants from aqueous systems include natural zeolites, clay minerals and biopolymers. The industrially produced adsorbents include activated carbon, chitosan, activated alumina, and silica gel. Moreover, these adsorbents have their specific applications (Vlaanderen, 2010). For example, natural clay

minerals are employed and are effective in the treatment of inorganic ions and highly polar organic ions through adsorption.

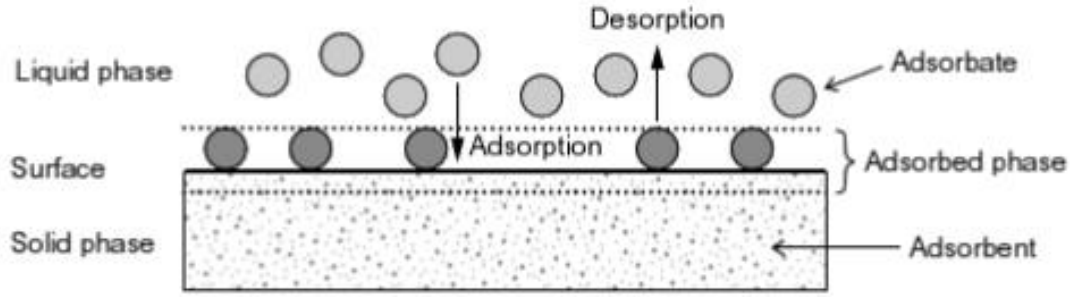


Figure 2-19: Adsorption's basic terminology presentation (Worch, 2012).

a. Adsorbents selectivity

The fundamental concern of the adsorption technique is to select an ideal adsorbent for the treatment and this depends on the adsorption equilibrium or adsorption kinetics (Ruthven, 1981). Most adsorption processes, however, are said to depend on equilibrium selectivity for the ideal adsorbents based on the separation factor (Ruthven, 1981). The separation factor measures the ease with which the adsorbate is separated from the solution, and the higher the separation factor, the greater the adsorptive capacity. The separation factor is represented by Equation 12.

$$\alpha_{AB} = \frac{X_A/X_B}{Y_A/Y_B} \quad \textbf{(12)}$$

where:

α_{AB} = separation factor

X_A and Y_A = substance A mole fraction in adsorbed and fluid phases at equilibrium.

b. Adsorbents

Despite high cost the industrially produced (engineered) adsorbents are said to achieve higher adsorptive capacities compared with the natural origin adsorbents (Ruthven, 1981; Worch, 2012). This is because the engineered adsorbents are produced with high quality control and have constant properties, while the properties of the natural origin adsorbents always exhibit significant variations, which contributes to their low adsorptive capacities (Worch, 2012). It is

the low-cost element of the natural origin adsorbents that draws the attention of scientists in employing the adsorption method as a treatment for wastewater and leachate. Some of the adsorbents and their applications are discussed below.

Zeolites

Zeolites are porous, crystalline aluminosilicates consisting of SiO_4 and AlO_4 tetrahedra groups connected together by oxygen atoms (Ruthven, 1981; Worch, 2012). Zeolites can be natural or synthetic. The general chemical composition of zeolite is written as $M_{x/n}[O.Al_2O_3.nSiO_2)].xH_2O$. Zeolites are mostly derived from silicates and carry a negative charge due to high number of Si (4) valence electrons (Worch, 2012). According to Ruthven (1981), there are about 38 identified frameworks of zeolite, which include both the natural and synthetic forms. There are different classes of zeolites (A, X, and Y) and each class depends on the molar Si/Al ratio (modulus *n*) (Worch, 2012). For example, zeolite A has modulus *n* of 1.5 to 2.5, zeolite X has *n* values between 2.2 and 3.0, and zeolite Y has modulus *n* of 3.0 to 6.0. These classes of zeolites are known to be hydrophilic, which means they are effective in ion exchange processes other than adsorption of neutral organic elements. According to Worch (2012), the hydrophilic character of zeolites depends on the modulus *n*: the hydrophilicity increases with increasing n. Zeolites with *n* value greater than 10 are said to be hydrophobic. It is this hydration property that makes zeolites very affinitive to NH_4^+ (Nguyen & Tanner, 1998).

As mentioned, the Si/Al ratio results in replacement of Si^{4+} by Al^{3+} causing the zeolite framework to possess an overall negative charge which requires balancing by exchangeable cations (Nguyen & Tanner, 1998). Greater substitution results in higher negative charge and therefore a greater number of cations is required to balance the negative charge. These exchangeable cations include Cs^+, K^+, NH_4^+, Na^+, Mg^{2+} and Ca^{2+} (Worch, 2012). The ability to exchange cations is also a fundamental property of zeolite used in adsorption applications, ionic exchange applications and ionic sieving. In addition, there are other vital properties that makes zeolite effective in ionic exchange and adsorption applications. These include high internal surface area, high porosity, low density and crystal stability (Nguyen & Tanner, 1998; Ruthven, 1981; Worch, 2012).

There are a number of natural zeolites, including modernite, clinoptilolite, erionite, chabazite and phillipsite (Nguyen & Tanner, 1998). These zeolites have been used worldwide in drinking

water and wastewater purification for removal of metals (iron, lead, manganese and nickel). They have also been found useful in improving agricultural land (Inglezakis, Vassilis, Zorpas, & Antonis, 2012). Therefore, this study investigated a natural New Zealand zeolite to check the best likely adsorption performance to use with local soils.

Other natural adsorbents

Other natural adsorbents that are low cost include: clays, peat, wood, coal and chitosan (Worch, 2012). Among the listed natural adsorbents, clays are highly regarded for adsorption due to their clay mineral property. According to Worch (2012), the clay mineral possesses a large negative charge that requires a large number of cations to balance the negative charge. This allows the clays to adsorb more positively charged ions from the cations such as Zn^{2+}, Cu^{2+}, K^{+}, NH_4^{+}, Mg^{2+} and Ca^{2+}. This high adsorption capacity characteristic makes clay a more effective adsorbent than others. Equation 13 shows a typical clay adsorption process.

$$\mathrm{ClayNa} + \mathrm{NH_4^+} \leftrightarrow \mathrm{ClayNH_4} + \mathrm{Na^+} \quad \textbf{(13)}$$

Equation 13 shows how the clay minerals bond with the ammonium ion by substituting the sodium ion. Clays have been used worldwide in removing heavy metals and dyes from industrial and textile wastewater respectively (Worch, 2012). Therefore, in view of the effectiveness and low cost of clays, this study investigated four different clay-containing local soils for the potential removal of NH_4^{+} from landfill leachate. These soils include: type A, type B, type C (from water supply dam) and type D (from silt dam). More details about these soils are in Chapter 5.

c. Cation exchange capacity (CEC)

The effectiveness of the adsorption process for soils is commonly measured as its cation exchange capacity of the soils. Cation exchange capacity (CEC) can be explained as the amount of cations that a soil can adsorb to balance its net negative charge particles (Daniel, Hinrich, & George, 2015). It is expressed as meq/100 g (milli-equivalents per 100 grams) of soil, and depends on pH and ionic strength (Robertson, Coleman, Bledsoe, & Sollins, 1999). The higher the clay mineral content, the higher the CEC and likewise the lower the clay mineral content (sandy soils) the lower the CEC. Moreover, water holding capacity for soils with high CEC is said to be greater than for soils with low CEC (Daniel et al., 2015). Equation 13 also describes

cation exchange reaction. The cation exchange capacity of different zeolites and other soil types are presented in Table 2-8 and Table 2-9. Zeolite soils with low Si/Al ratio present high CEC (chabazite, zeolite A, X, and Y) as shown in Table 2-8 while clays and humus soils exhibit high CEC as shown in Table 2-9.

Table 2-8: Different Zeolites and Their Cation Exchange Capacity. Adapted from (Ralph, 2003).

Zeolite	**Si/Al ratio**	**Meq/g (anhydrous)**
Chabazite	2.0	5.0
Mordenite	5.0	2.6
Erionite	3.0	3.8
Clinoptilolite	4.5	2.6
Zeolite A	1.0	7.0
Zeolite X	1.25	6.4
Zeolite Y	2.0	5.0

Note. Retrieved from Adsorbents: Fundamentals and applications book. Copyright 2003 by Ralph. Reprinted by permission.

Table 2-9: Different Soils and Their Cation Exchange Capacity. Adapted from (Donahue, Miller, & Shickluna, 1977).

Soil	**CEC meq/100 g**
Sands	1–5
Fine sandy loams	5–10
Loams and silt loams	5–15
Clay loams	15–30
Clays	over 30
Sesquioxides	0–3
Kaolinite	3–15
Illite	25–40
Montmorillonite	60–100
Vermiculite (similar to illite)	80–150
Humus	100–300

Note. Retrieved from An Introduction to Soils and plant growth book. Copyright 1977 by Donahue and Miller. Reprinted by permission.

d. Adsorption types

There are two types: physical and chemical adsorption (Ruthven, 1981; Worch, 2012). Physical adsorption occurs when there are weak van der Waals forces of attraction between the adsorbent and adsorbate forming a weak bond between the two (Ruthven, 1981; Worch, 2012). In contrast, chemical absorption occurs when there is a chemical bond between the adsorbent and adsorbate (Ruthven, 1981; Worch, 2012).

e. Factors affecting adsorption rate

Several factors influence adsorption by a solid, such as surface area, nature of adsorbent and adsorbate, pH of the solution, distribution of adsorbent pore size, temperature and mixed solutes (Ruthven, 1981; Worch, 2012). Some of these factors are discussed below.

External and internal surface area: According to Worch (2012) surface area influences adsorption in two ways (external and internal surface area). During adsorption, the external surface area influences the mass transfer rate. The smaller the external surface area, the lower the rate of mass transfer, hence low adsorption occurs. The internal surface area of the

adsorbent, however, is the one that provides its adsorption capacity (Worch, 2012). This parameter (internal surface area) is said to be the most important parameter of the adsorbent: the higher the internal surface area of the adsorbent, the greater the adsorption capacity (Worch, 2012). In the main, the internal surface area of the engineered adsorbents exceeds their external surface area, which is a fundamental characteristic that makes them good adsorbents. Table 2-10 shows a typical range of internal surface area for different adsorbents.

Table 2-10: Different Adsorbents and Typical Ranges of Internal Surface Area (Worch & Eckhard, 2012)

Adsorbents	**Range of Internal surface area** (m^2/g)
Activated carbons	600–1,200
Polymeric adsorbents	300–1,400
Aluminium oxides	150–350
Granular ferric hydroxides	150–350
Zeolites	400–900

Note. Retrieved from Adsorption Technology in Water Treatment: Fundamentals book. Copyright 2012 by Eckhard Worch.

Distribution of pore size: There are three types of pore size distributions that can be used to differentiate adsorbents: micropores, mesopores and macropores as shown Table 2-11 (Worch, 2012). According to Worch (2012) mesopores and macropores influence the rate of mass transfer of the adsorbate particles, while the volume influences the adsorbent's internal surface area hence the capacity of the adsorbent (Worch, 2012).

Table 2-11: Categories of Pores (adapted from Worch, 2012)

Pore class	**Range of pore radius** (nm)
Micropores	< 1.0
Mesopores	1–25
Macropores	> 25

pH

Adsorption is influenced greatly by the pH of the adsorbate because of the hydroxide and hydrogen ions that are attached (Worch, 2012). The hydroxide and hydrogen ions in the solution tend to compete with other ions during the adsorption process, hence lowering the adsorption capacity. If the pH of the solution is low it affects the distribution of the ions hence greatly affects the adsorption equilibria (Worch, 2012).

Temperature

The effects of temperature are not really significant in the range (10 to 30°C) of most environmental conditions (Worch, 2012).

f. Adsorption equilibria

Adsorption equilibrium is used to assess the effectiveness of the adsorption processes and adsorber design (Ruthven, 1981). To assess the adsorption system, and hence the performance of the adsorbent, equilibrium models (adsorption isotherms) are used. These adsorption isotherms include linear, Freundlich and Langmuir isotherm equations and this study utilised the linear isotherm.

The linear isotherm is also referred to as Henry's Law and is the simplest adsorption isotherm in which the fluid and adsorbed phase concentrations have a linear equilibrium relationship (Ruthven, 1981). Most practical isotherms use the linear isotherm to describe their initial parts. The Henry's Law utilises the adsorption equilibrium constant known as Henry's constant which is expressed as concentration or pressure.

$$\mathrm{q} = Kc \tag{14}$$

where:

q = amount of adsorbate adsorbed per unit adsorbent

c = residual solute concentration

K = Henry's adsorption constant

The Henry's adsorption constant can be derived from the surface concentration (n_s).

$$n_s = \frac{K}{\mathcal{A}} c \tag{15}$$

where: n_s = surface concentration, $\mathcal{A}$ = specific area per unit volume of the asdsorbent

2.9.2 Biological nitrification removal

a. Introduction

There are different ways nitrogen (in the form of ammonia nitrogen) can be removed from wastewaters: physico-chemical and biological methods. These methods can be used individually or in combination. Moreover, the removal of ammonia nitrogen from wastewater depends on the characteristics of the wastewater (van Loosdrecht et al., 2016). For example, wastewater with concentrations of ammonium higher than 5 g N L^{-1} are treated by preference with physico-chemical methods, while biological methods are preferred for ammonium concentrations lower than 100 mg N L^{-1}. With the biological methods, the COD/N ratio of the wastewater is often used to determine the appropriate biological method to be employed (van Loosdrecht et al., 2016). For example, for wastewater with COD/N ratio less than 5 g COD g N^{-1}, nitrification-anammox or nitrite routes are used to lower ammonia nitrogen to satisfactory levels; for wastewater with COD/N ratio between 5 and 20 g COD g N^{-1} a combination of nitrification, microbial growth nitrogen assimilation and heterotrophic denitrification is used; for wastewater with COD/N ratio greater than 20 g COD gN^{-1}, nitrogen assimilation of heterotrophic bacteria for biomass synthesis during COD (organic matter) removal is used to lower the ammonia nitrogen to satisfactory levels.

This study investigated the potential of removing ammonia nitrogen from landfill through nitrification method as explained in Chapter 6. An overview of the nitrification method is discussed below.

b. Nitrification

Nitrification is a biological process whereby ammonium is converted to nitrate by a specialised group of aerobic bacteria (Mihelcic & Zimmerman, 2013; van Loosdrecht et al., 2016). This method is divided into two processes. The first process involves the conversion of ammonia and ammonium to nitrite by a group of bacteria called *Nitrosomonas.* This nitrification process is shown by a catabolic macro-chemical reaction shown in Equation 16. The second stage involves the oxidation of nitrite to produce nitrate through another group of bacteria called *Nitrobacter* as shown in Equation 17. These groups of bacteria derive their carbon source from inorganic carbon for synthesis of organic molecules and their energy from ammonia and nitrogen sources (van Loosdrecht et al., 2016). Moreover, these groups of bacteria (nitrifies) only perform nitrification under aerobic condition. That means they require adequate dissolved

oxygen of 0.5 mg/L or more (Mihelcic & Zimmerman, 2013). According to Mihelcic and Zimmerman (2013) and van Loosdrecht et al. (2016), dissolved oxygen values lower than 0.5 mg/L will inhibit the growth rate of nitrifiers.

$$\mathrm{NH_4^+ + OH^- + \ 1.5}O_2 \rightarrow NO_2^- + H^+ + 2\mathrm{H_2O} \quad \textbf{(16)}$$

$$\mathrm{NO_2^-} + 0.5O_2 \rightarrow NO_3^- \quad \textbf{(17)}$$

Other requirements necessary for the nitrification process include:

- retention time that is long
- enough food to microorganism
- high residence time
- adequate buffering (alkalinity between 50 to 100 mg/L)
- pH near 7.0
- temperature between 10 and 35ºC

c. Nitrification inhibitors

Acid is produced during the nitrification process, which then lowers the biological population's pH (van Loosdrecht et al., 2016). This low pH tends to inhibit the nitrification process. According to van Loosdrecht et al. (2016) the nitrifiers (bacteria) thrive at pH values between 7.5 and 8.5 but nitrification process stops at pH below 6.0. However, the nitrification process does take place effectively at pH values between 6.5 and 7.0 in most treatment plants. Moreover, levels of free ammonia are increased by high pH (> 8.5) and temperature (> 40ºC) of the biological population, which lead to nitrification inhibition (Yusof et al., 2010). There are other inhibitors to nitrification that are toxic to *Nitrosomonas* and *Nitrobacter*, such as heavy metals (mercury, silver, nickel, copper, chromium and zinc), phenol, thiourea and cyanide (van Loosdrecht et al., 2016). In addition, high concentration of free ammonia and nitrous acid also inhibits the nitrifiers, therefore stopping the nitrification.

2.10 Previous studies of ammonia nitrogen removal by coagulation–flocculation

According to previous studies it is evident that removal of ammonia nitrogen by coagulation–flocculation has been less well studied and also proven very challenging. This is because most nitrogen in leachate is not in the form of colloids; therefore, the potential to remove the ammonia nitrogen by coagulation–flocculation is not as high. The few studies that have examined ammonia nitrogen removal by coagulation–flocculation are presented below.

2.10.1 Coagulation–flocculation in leachate treatment by using ferric chloride and alum as coagulant by Rui et al. (2012)

Rui et al. (2012) conducted a study using the coagulation–flocculation method in treating a stabilised landfill leachate using ferric chloride ($FeCl_3$) and aluminium sulfate (alum). Their study examined the coagulants used and compared the results with respect to ammonia nitrogen, suspended, COD and colour removals. The leachates used were sampled from Pasir Gudang sanitary landfill in Malaysia and had high ammonia nitrogen concentrations in the range of 1,350 mg/L to 2,150 mg/L. The average concentrations of COD and BOD5 were 2,305 mg/L and 131.5 mg/L respectively with a BOD5/COD ratio of about 0.05. This was an old or stabilised leachate with high pH values of greater than 7.5. A conventional jar test experiment was employed in trying to optimise variables such as pH, coagulant dose, rapid and slow mixing and settling time. Optimisation was based on the maximum percentage removal of the leachate constituents and determined after coagulation–flocculation. The results are presented below.

The effect of rapid speed and rapid mixing time on the treatment was analysed for both ferric chloride and alum. The mixing speed and mixing time varied from 70 to 300 rpm and 1 to 6 minutes respectively while the settling time was kept constant at 30 minutes. The results of both the coagulants are presented in Figure 2-20 and Figure 2-21. Figure 2-20 shows the effects of different speed and duration on ferric chloride and alum coagulants with respect to the removal of ammoniacal nitrogen, COD, colour and SS. The rapid mixing time (3 minutes) and speed (150 rpm) achieved maximum ammoniacal nitrogen percentages removals of 22% and 26% respectively. While alum (Figure 2-21) achieved the maximum ammoniac nitrogen percentages removals of 5% and 7% rapid mixing time (3 minutes) and speed (150 rpm) respectively.

The effect of pH on each coagulant was also examined. Figure 2-22 show the effects of pH on each coagulant with respect to the removal of ammonia nitrogen, COD, colour and SS. The maximum ammonia nitrogen percentages removal of 26% was achieved with ferric chloride at pH 7, as shown in Figure 2-22 (a). Alum, however, achieved a maximum of 14% of ammoniacal nitrogen at pH 7, as shown in Figure 2-22 (b). Moreover, still at pH 7, ferric chloride achieved higher removals of COD (28%), colour (82%) and SS (92%) while alum removed 33% COD, 78% colour and 68% SS.

The effect of coagulant dose was also examined for each coagulant. Figure 2-23(a) shows that ferric chloride achieved a maximum ammonia nitrogen percentage removal of 26% at a dose of 3,500 mg/L, while alum Figure 2-23(b) achieved maximum ammonia nitrogen percentages removal of 24% at a high dose of 9,000 mg/L.

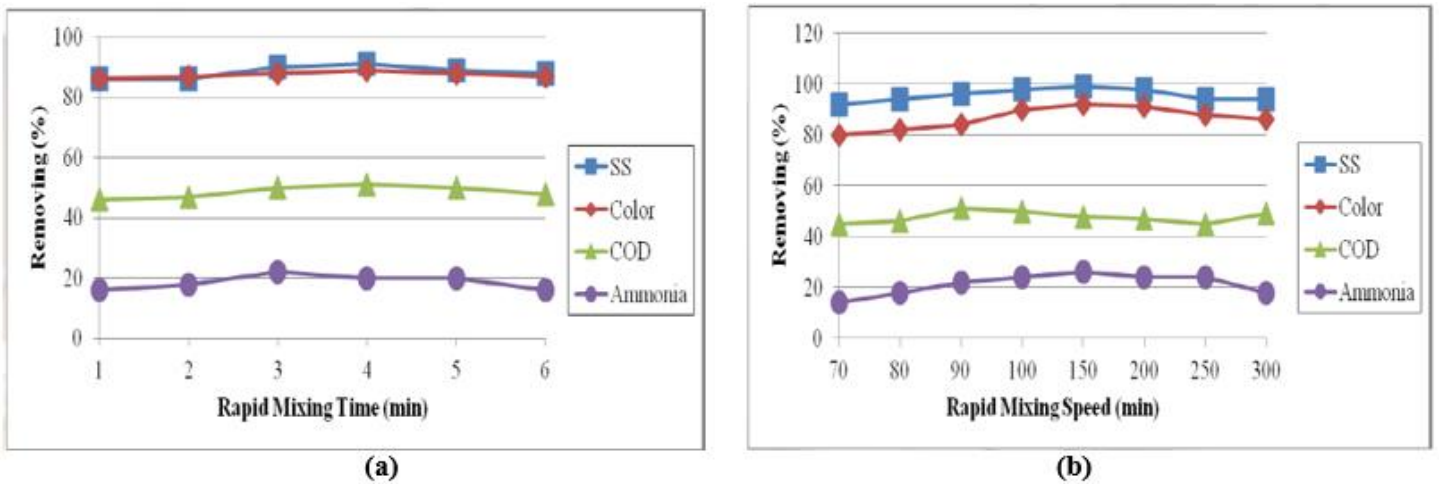


Figure 2-20: Effect of mixing speed and mixing time with ferric chloride. (a) Rapid mixing time varied from 1 to 6 minutes with ferric chloride. (b) Rapid mixing speed varied from 70 to 300 rpm with ferric chloride. Adapted from Rui et al. (2012).

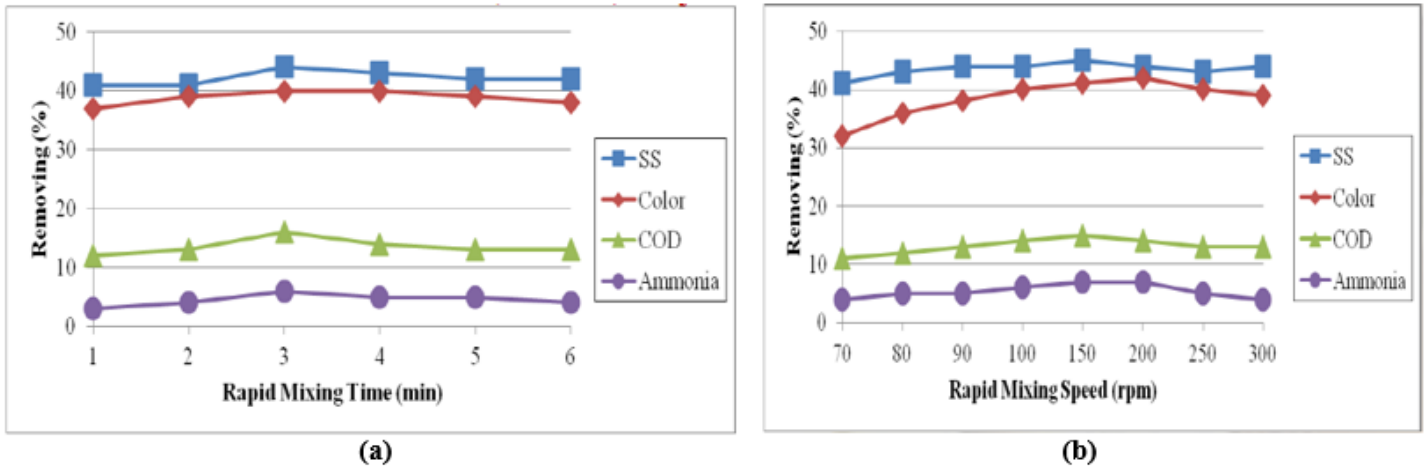


Figure 2-21: Effect of mixing speed and mixing time with alum. (a) Rapid mixing time varied from 1 to 6 minutes with ferric chloride. (b) Rapid mixing speed varied from 70 to 300 rpm with ferric chloride Adapted from Rui et al. (2012).

48

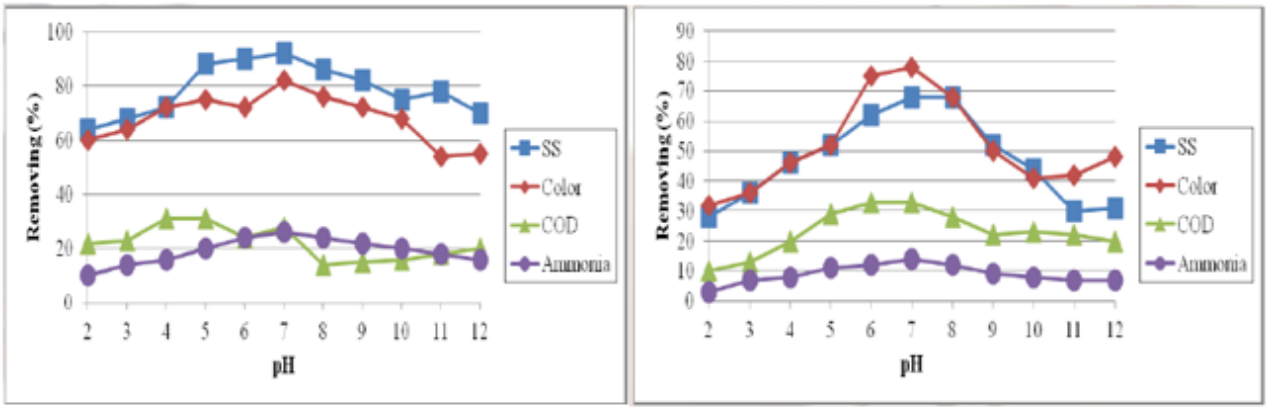


Figure 2-22: Effect of pH on treatment. (a) Pollutants percentage removals with ferric chloride. (b) Pollutants percentage removals with alum. Adapted from Rui et al. (2012).

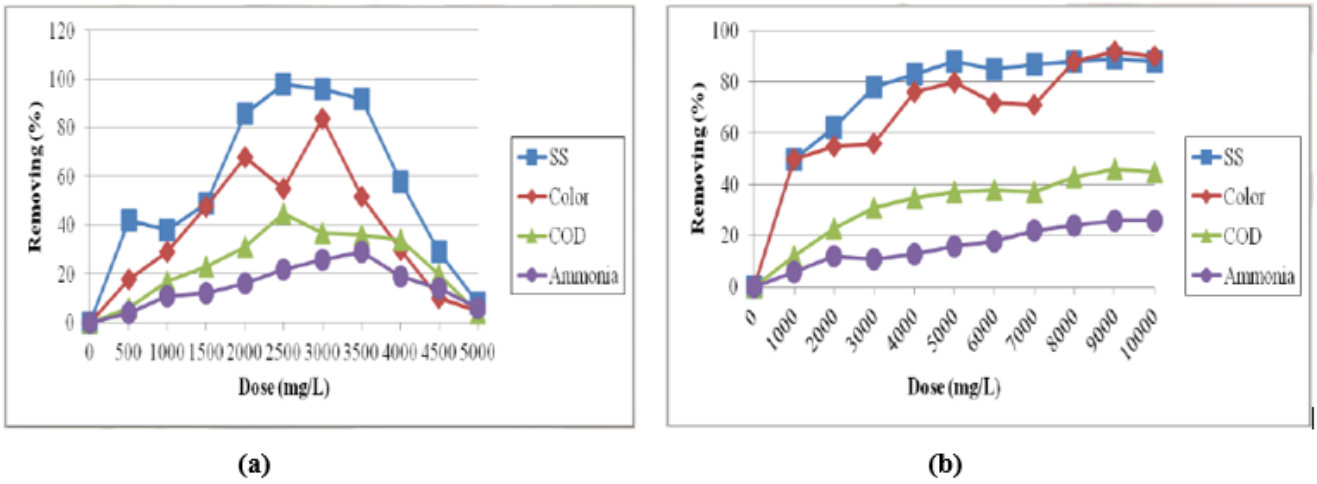


Figure 2-23: Effect of coagulant dose on treatment. (a) Pollutants percentage removals with ferric chloride. (b) Pollutants percentage removals with alum. Adapted from Rui et al. (2012).

Rui et al. (2012) achieved a maximum ammonia nitrogen percentages removal of 26% with ferric chloride at a dose of 3,500 mg/L and at pH 7. However, the study did not remove ammonia nitrogen effectively, compared with the removal of COD, colour and SS. This could be because most nitrogen in leachate is not in the form of colloids in contrast to other pollutants, hence the potential to remove ammonia by flocculation is not as high. Moreover, optimisation of other conditions were not thoroughly examined to focus on ammonia nitrogen removal.

2.10.2 Treatment of landfill leachate by using lateritic soil as a natural coagulant

Syafalni et al. (2012) conducted a study using coagulation–flocculation to treat a stabilised landfill leachate using lateritic (iron-rich) soil and aluminium sulfate (alum). The research examined the coagulants used and compared the results with respect to ammoniacal nitrogen, SS, COD and colour removals. The leachate used was sampled from Byram Forest Reserve Area in Malaysia. This had very high concentrations of COD and ammoniacal nitrogen of about 3,500 mg/L and 2,040 mg/L respectively, as shown in Table 2-12. The lateritic soil used was from a topsoil layer with high carbon and iron contents of 5.94% and 6.44% respectively. A conventional jar test experiment was employed in this study. Rapid and slow mixing and settling time were kept constant.

Table 2-12: Penang Landfill Leachate Characteristics (Syafalni et al., 2012).

Parameter	Range	Mean	Effluent (standard B)[a]	S.D.[b]
pH	8.30–8.45	8.38	5.5–9.0	0.11
Temperature (°C)	25–31	28	40	4.24
COD (mg/L)	2950–4050	3500	100	777.82
Color (PtCo)	4650–4850	4750	–	141.42
Total solids (mg/L)	9790–9950	9870	–	113.14
Total suspended solids (mg/L)	86–298	192	100	149.91
Turbidity (NTU)	58–74	66	–	11.31
Ammoniacal-nitrogen (mg/L)	1820–2260	2040	–	311.13

[a] Environmental Quality (Sewage and Industrial) regulations, 1979 (MDC, 2006).
[b] Standard Deviation.

The maximum ammonia nitrogen percentages removal of 47.6% was achieved with alum at optimal pH 4.8 and an alum dose of 10,000 mg/L, while lateritic soil achieved a maximum of 41.2% of ammonia nitrogen at pH 2.0 and soil dose of 14,000 mg/L. These experiments were conducted at very low pH (4.8 and 2.0) conditions which is very impractical and challenging. Moreover, optimisation was not conducted.

2.10.3 Nutrient removal and sludge production in the coagulation–flocculation process

Aguilar, Sáez, Lloréns, Soler, and Ortuño (2002) conducted a study using a coagulation–flocculation process in the removal of nutrients from slaughterhouse wastewater. The coagulants used in this study were ferric sulfate, aluminium sulfate and polyaluminum chloride. In addition, various coagulant aids (inorganic and synthetic polyelectrolytes) were coupled with coagulants in order to achieve maximum treatment. The coagulant aids used included powdered activated carbon, activated silica, precipitated calcium carbonate, cationic polyacrylamide, polyvinyl alcohol, anionic polyacrylamide and polyacrylic acid. The slaughterhouse wastewater used in this study had a 22.1 mg/L average concentration of ammonia nitrogen. In addition, the average concentrations of Total Kjeldahl Nitrogen (TKN), albuminoid nitrogen, COD and BOD5 was measured to be 71.7 mg/L, 56.9 mg/L, 5,398 mg/L and 2,763 mg/L respectively. A conventional jar test experiment was employed in this study and the supernatant was analysed for ammonia nitrogen, TKN and albuminoid nitrogen.

The dose and optimal pH values for each coagulant were as follows: ferric sulfate was 500 mg Fe^{3+}/L and pH 7.0, aluminium sulfate was 600 mg Al^{3+}/L and pH 5.0, and polyaluminum chloride was 857 mg Al^{3+}/L and pH 6.0–7.0. The doses of the coagulant aids were variable. The ammonia nitrogen reductions achieved by this study with all the coagulants and coagulants aids was less than 17%. The TKN reductions varied from 50% to 70% with various coagulant aids, while the reductions of albuminoid nitrogen were high (74% to 83%).

The research by Aguilar et al. (2002) did not effectively remove ammonia nitrogen, achieving reductions of less than 17% with various coagulants and coagulant aids. However, very significant TKN reductions (50% to 57%) were recorded with various coagulant aids. In addition, high reductions of albuminoid nitrogen (74% to 83%) were obtained with various coagulant aids. According to Aguilar et al. (2002) the reduction of ammonia nitrogen and TKN is associated with either the pollutants attaching to the salt precipitates or attaching to the surface of the (negatively charged) colloids due to electrostatic attraction forces. Moreover, this study explains that the reason for high albuminoid nitrogen reductions is because it is in the form of proteins in water which are partially hydrophobic and partially hydrophilic. Ammonia nitrogen removal proved to be challenging, and optimisation was not conducted in this study.

CHAPTER 3. Analytical methods and leachate characterisation

3.1 Introduction

This chapter discusses the sampling method, analytical methods and the characteristics of the landfill leachate used for this study. The objective of characterising landfill leachate is to estimate its pollution potential and identify types of possible treatment. For example, in this study ammonia nitrogen is the parameter of concern and the goal is to identify treatments suitable to reduce its concentration, consequently minimising its adverse impact on the environment and treatment plants. The overall physico-chemical parameters analysed in this study include pH, turbidity, total alkalinity, conductivity, salinity, ammonia, total nitrogen, COD, colour, total suspended solids (TSS), TS, nitrates and nitrites.

3.2 Materials and method

3.2.1 Leachate sampling and analysis

The landfill leachate samples were collected from a landfill situated in the Canterbury region, in the South Island of New Zealand. The site has an area of about 37 hectares, receiving about 1,200 tonnes of solid waste daily. The type of solid waste at this landfill is MSW that comes from domestic housing, markets, construction, institutions and industry (CAE, 2000). A typical waste composition for the landfill in question is shown in Figure 3-1. The site is equipped with a series of 30, 000 litre-capacity leachate storage tanks and the samples were drawn manually into well-labelled 25 L plastic containers (Figure 3-2). The containers were then transported immediately to the University of Canterbury environmental laboratory and stored at 4°C while awaiting analysis. Leachate sampling was done when necessary to minimise the possibility of sample biodegradation or volatilisation. Leachate sampling, preservation and analytical methods followed the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, & WFE, 2005).

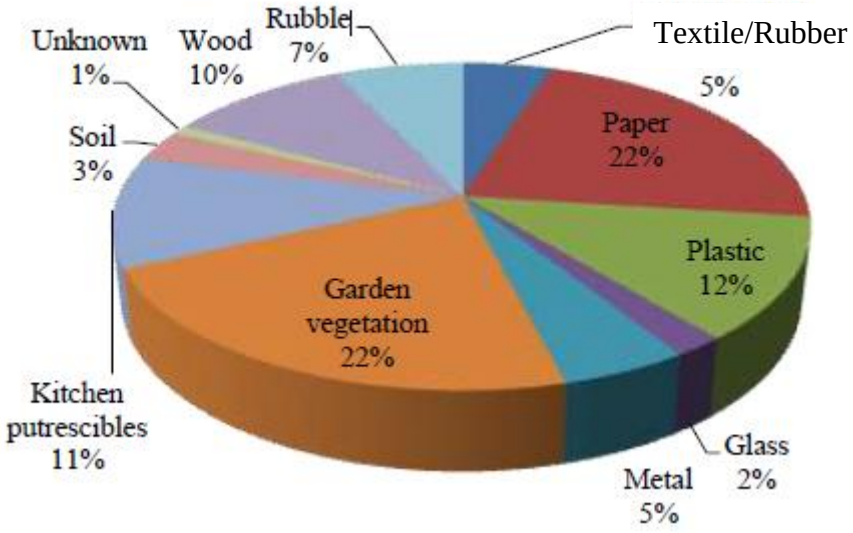


Figure 3-1: Christchurch City Council waste composition (adapted from CAE, 2000).

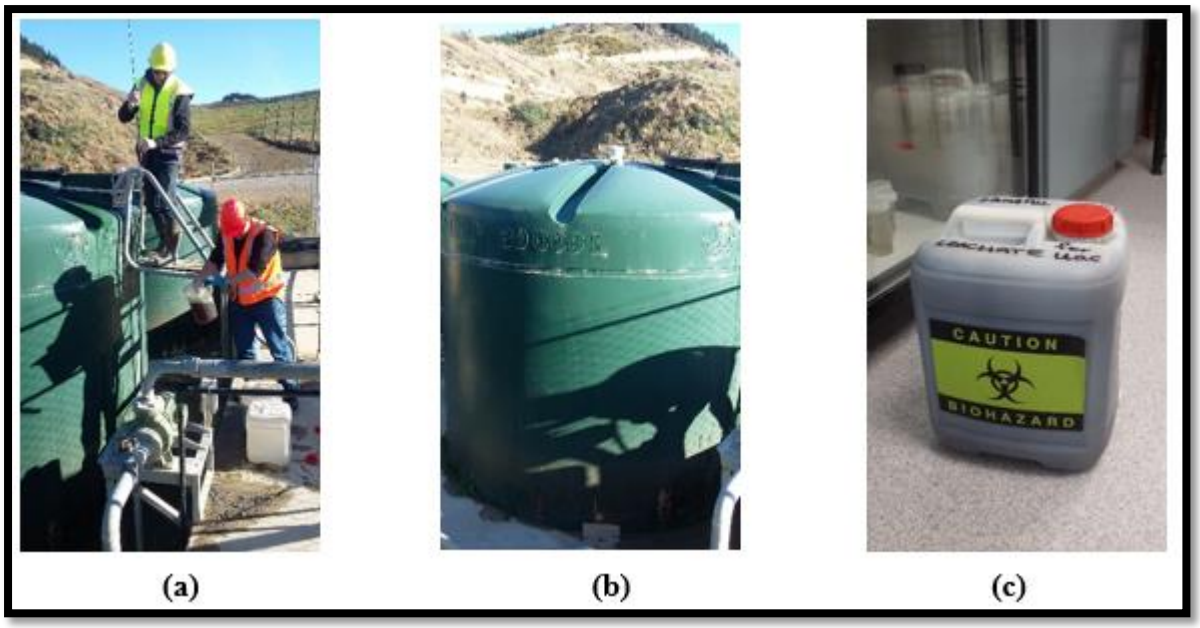


Figure 3-2: (a) Landfill staff assisting with drawing leachate samples from the storage tanks. (b) Site leachate 30 000 L storage tanks. (c) Well-labelled 25 L leachate container ready for storing and analysis.

3.3 Analytical methods

3.3.1 Landfill leachate characterisation

All the leachate samples were analysed and characterised in the University of Canterbury environmental laboratory based on the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005). Before characterising the leachate, filtering using a disposable 0.45 micron syringe was performed to remove coarse suspended solids. The refrigerated samples were allowed to reach ambient temperature (this took about 2 hours) before any analysis. Thereafter the leachate samples were analysed for pH, turbidity, total alkalinity, conductivity, salinity, ammonia (NH_3-N), Total Kjeldahl Nitrogen (TKN), Chemical Oxygen Demand (COD), colour, Total Suspended solids (TSS), Total Solids (TS), nitrates (NO_3 – N) and nitrite (NO_2 – N). The analytical method for each physico-chemical parameter is explained in detail below.

a. pH

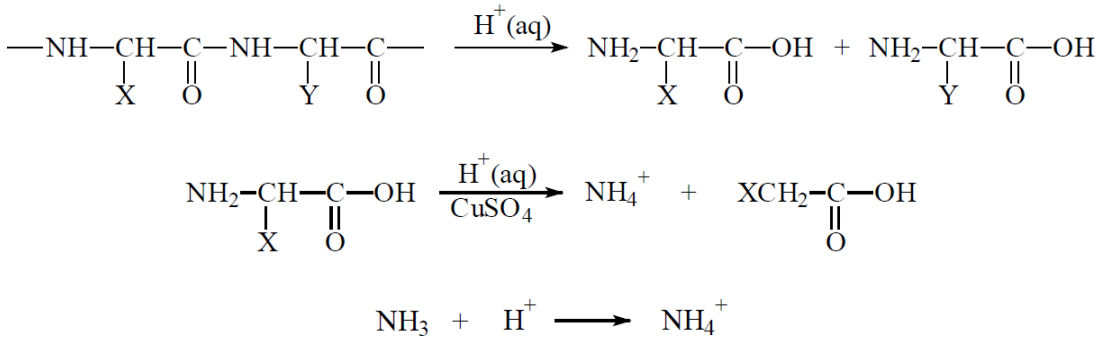
All pH measurements were conducted using a pH meter – EDT instruments microprocessor (RE 357-Tx). The pH meter calibration was performed before the start of each day (due to demand by other researchers) or prior to each measurement for extreme precision when necessary. Calibration was performed with three buffers (pH 4.0, 7.0 and 10.0) and precautions were taken to ensure the buffers were fresh. In addition, calibration was performed every time before taking pH measurements. Accuracy was estimated at ± 0.05 (APHA et al., 2005).

Where applicable, the pH was adjusted prior to a treatment test. Adjustments were performed either using 1.0N (normality) hydrochloric acid (HCl) and 1.0N sodium hydroxide (NaOH). Care was taken to ensure stabilisation of the meter reading before adding more base or acid.

b. Total Kjeldahl Nitrogen (TKN)

Total nitrogen tests were determined using the Kjeldahl method 4500-N based on the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005). The Kjeldatherm TZ- controller and Vapodest 4s, Gerhardt were used to determine both ammonia and organic nitrogen levels in three stages: digestion, neutralisation and distillation. The first part entails digesting the leachate sample up to 400 °C to form $(NH_4)_2SO_4$ with the help of a copper sulfate catalyst. Digestion converts organic nitrogen into NH_4^+ ions as shown in Equations 15 and 16 below. The second part (neutralisation) converts NH_4^+ ions to NH_3 by changing from acid

conditions to alkali conditions with the addition of sodium hydroxide (NaOH) as shown in Equations 18 and 19 (Thomas & Paris, 1989). The final stage – distillation – causes the NH_3 to escape as it reacts with boric acid. A titrimetric method was then used to determine the organic nitrogen concentrations in the solutions. For quality control, about 1000 mg/L NH_3-N was made up with 3.819 g/L of ammonium chloride and all the tests were held to an accuracy of ± 50.0 mg/L during quality control checks.



(18)

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \quad \textbf{(19)}$$

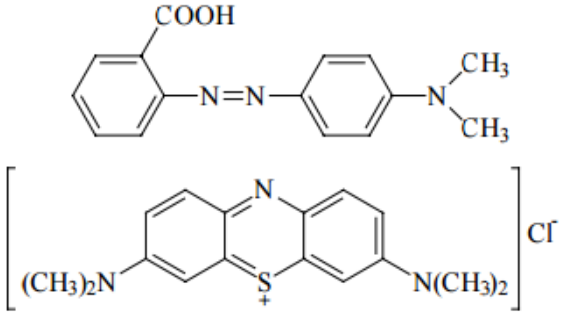
c. Ammonia concentrations

In this study, two methods were used for determination of ammonia concentration: the salicylate method and the distillation–titration method. The salicylate method was conducted according to Method 10031, based on HACH (2002). This method measures low concentrations of ammonia within a range of 0.4 to 50.0 mg/L of NH_3-N. A blank sample of deionised water with 0 mg/L of NH_3-N was measured in all the samples. For quality control about 1000 mg/L NH_3-N was made up with 3.819 g/L of ammonium chloride, and all the test were made to an accuracy of ± 50.0 mg/L as a check of quality control.

The distillation and titration method was used to determine higher NH_3-N concentrations using the Micro-Kjeldahl method 4500-N based on the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005). The 20 mL leachate sample was buffered, using a borate buffer, to keep the solution at pH 9.2. About 70 mL of 6N NaOH solution was used to adjust the pH to 9.2. This was to reduce or prevent hydrolysis of organic nitrogen and cyanates to NH_3. An addition, of 100 mL of deionised water was also added to help the sample to boil. Titration was against sulfuric acid (H_2SO_4) using a combined indicator of methylene blue and methyl red (pKa = 5.0) to determine the NH_3-N concentrations in the solutions. Equation 20

shows NH_3 being given off after titration using borate buffer and distillation process. For quality control, about 1,000 mg/L NH_3-N was made up with 3.819 g/L of ammonium chloride and all the tests were conducted to accuracy of ± 50.0 mg/L as a check of quality control.

$$Na_2B_4O_7{\cdot}10H_2O(s) \rightarrow 2Na^+ + 2B(OH)_3 + 2B(OH)_4^- + 3H_2O$$
$$B(OH)_3 + 2H_2O \_ B(OH)_4^- + H_3O^+$$



(20)

The amount of the titrant used in the distillation–titration method was converted into the NH_3-N concentration (in given units here) using the following formula:

$$NH_3 - N = \frac{(\text{titrant} - \text{blank}) * N * 14007}{Sample\ volume\ (mL)} \quad \textbf{(21)}$$

where:

N = normality of sulfuric acid (H_2SO_4)

Titrant = the amount of H_2SO_4 used for titrating with leachate sample (ml)

Blank = the amount of H_2SO_4 used in titrating with di-ionised water (ml)

d. Chemical oxygen demand (COD)

COD measures the total amount of oxygen required for oxidising materials in a sample. A modified method based on HACH (2002) was used for measuring COD in this study. This method makes use of a COD high range digestion solution and Program number 9000 on the DR3900 spectrophotometer. A standard curve was created on this program using average absorbance values from different standards as a COD test guide. Due to high concentration of the COD in the leachate sample, the sample was diluted to 10% and 20% to enable reading by the spectrophotometer. The spectrophotometer only measures to a maximum of 1200 mg/L of COD concentrations while the leachate sample contained over 4,000 mg/L. In every batch a

blank and duplicates of quality control (COD standard of 600 mg/L) were conducted for every COD test to preserve accuracy. All the tests were conducted to accuracy of ± 50.0 mg/L as a check of quality control.

e. Turbidity

Turbidity can be defined as a measure of the presence of colloidal and suspended particles including clay and microorganisms in water or solution. The leachate sample was analysed for turbidity with a turbidimeter (HACH model 2100P). A Gelex standard of range 0–100 (nephelometric turbidity units) NTU was used for quality control. Importantly, HACH StablCal standards were used for the calibration of the turbidimeter using Nephelometric method 2130B based on the based on the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005). Figure 3-3 shows the turbidity test apparatus used in this study. All the tests were conducted to accuracy of ± 0.50 mg/L as a check of quality control.

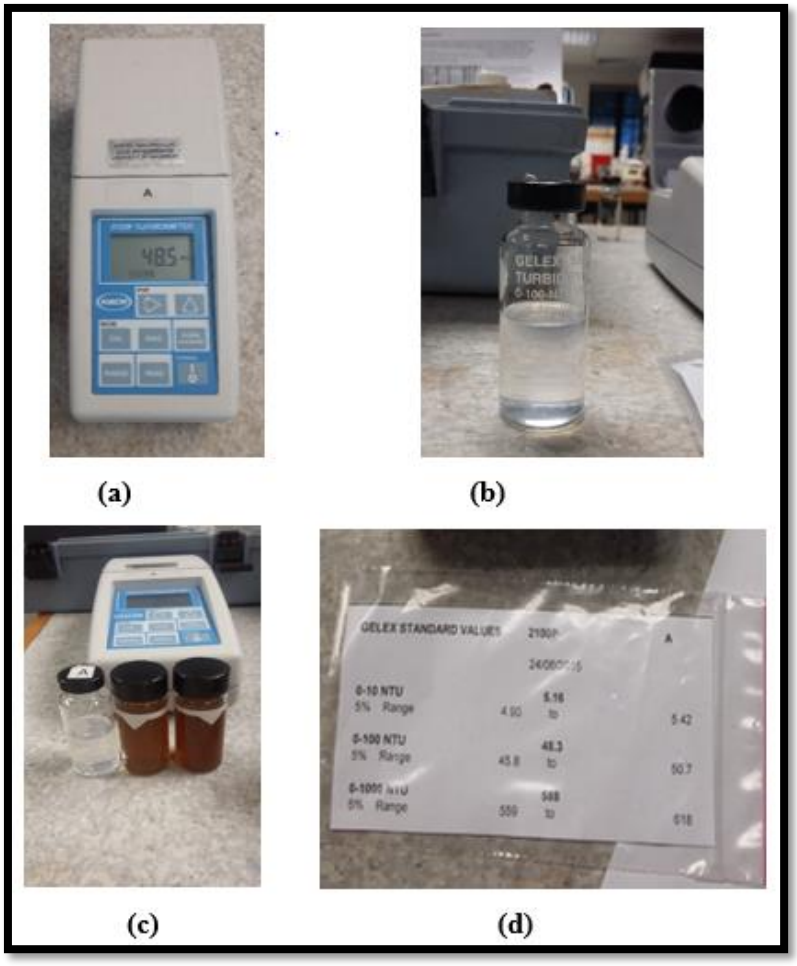


Figure 3-3: (a) HACH model 2100P turbidimeter (b) A 0 – 100 NTU gelex standard. (c) Leachate samples and gelex standard ready for analysis on a turbidimeter. (d) Gelex standard values for quality control.

f. Conductivity

The leachate sample conductivity was recorded using a YSI salinity conductivity temperature meter (Model number 30-10 FT). The conductivity was read as specific conductance at 25 °C and displayed in μS/cm, while salinity was displayed in mS. Stabilisation time was allowed for about 10 seconds before taking the readings after submerging the probe in the leachate solution. Calibration was performed with a 0.01M KCL conductivity standard each time before the instrument was used. For these experiments, ± 50 μS/cm values were considered accurate and sufficient for quality control.

g. Total suspended solids (TSS)

TSS measurement was performed according using method 2540D of the APHA Standard Methods for the Examination of Water and Wastewater. Duplicates of 100 mL blank (deionised water) samples were filtered through fibreglass filter papers and dried in the Contherm Thermotec 2000 oven at 103 to 105ºC for two hours. Thereafter, the dried glass filter paper was placed in the desiccator to cool down to room temperature, then weighed on a Mettler Toledo (ME204) analytical balance, and the mass of the filter was recorded. Multiple leachate samples of 100 mL each were weighed and filtered through the fibreglass filter and oven dried at 103 to 105 ºC for two hours. The filter papers were then cooled to room temperature in the desiccator and the mass of each was then found and recorded as mass sample + filter paper. All the tests were conducted to accuracy of ± 0.05 mg/L as a check of quality control. The leachate sample suspended solids (mg/L) was calculated as:

$$(\text{TSS}) = \frac{[\,(C - A) - D] * 10^6}{\text{sample volume}} \quad \textbf{(22)}$$

where:

C = mass sample + filter post evaporation (g)

A = mass filter (g)

D = solid loss/gain (g)

Figure 3-4 shows the TSS test apparatus and steps used in this study.

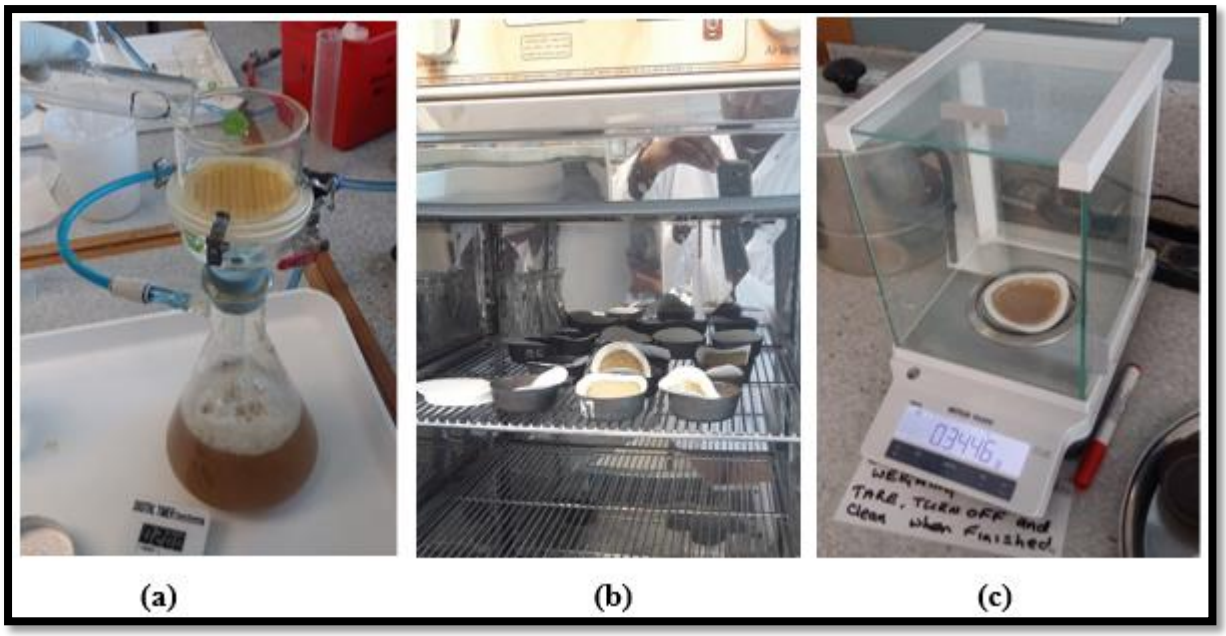


Figure 3-4: TSS procedure: (a) TSS set-up, (b) samples drying in an oven, (c) measuring on the analytical balance.

h. Total Alkalinity

The alkalinity of each leachate sample was measured using method 2320B of the APHA Standard Methods for the Examination of Water and Wastewater. The titration method was used with a standard 0.1N hydrochloric acid. This method requires titrating the 200 mL leachate sample down to a pH of about 4.5. The pH meter used–EDT instruments microprocessor (RE 357-Tx) was calibrated with three buffers (pH 4, 7 and 10) before use. The readings were allowed to stabilise for at least 10 seconds before recording, and for quality control, accuracy was kept at ± 0.02 (APHA et al., 2005). Figure 3-5 shows the alkalinity test apparatus and steps used in this study. The alkalinities of the leachate samples were then found using the equation as:

$$\text{Alkalinity expresses as } \frac{\text{mg}}{\text{L}}\text{CaCO}_3 = \frac{\text{A x N x 50,000}}{\text{mLsample}} \quad \textbf{(23)}$$

where:

A = mL of standard acid (HCI)

N = Normality of standard acid (HCI)

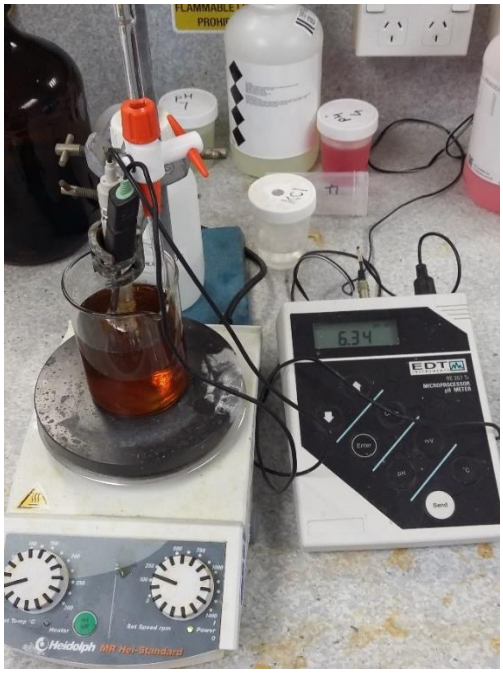


Figure 3-5: Total alkalinity set-up as performed.

i. Nitrates

For all the samples, nitrates tests were performed using the cadmium reduction method (method 8039) Program 355 N, nitrate HR based on HACH (2002). This method measures nitrate concentration from a sample within the range of 0.3 to 30.0 mg/L $N0_3$–N. A blank sample of deionised water was used as a check of accuracy. Prior to measurements, the leachate sample was filtered through filter crucibles of average pore size 40 μm to avoid turbidity interference. Also, the powder pillows (NitraVer 5 Nitrate) was thoroughly dissolved by shaking for one minute, and was left for five minutes undisturbed (the reaction time). The outsides of the vials were thoroughly wiped before insertion into the DR 3900 spectrophotometric instrument for reading. For quality control the tests are read to ± 0.05 mg/L.

j. Nitrites

Nitrite tests were performed using the ferrous sulfate method (Method 7153) Program 373 N, nitrate HR based on HACH (2002). This method measures nitrite concentration from a sample within the range of 2 to 250 mg/L NO_2^-. A blank sample of deionised water was used as a check of accuracy. Prior to measurements, the leachate sample was filtered through filter crucibles of average pore size 40 μm to avoid turbidity interferences. Also, the reagent powder pillows (Nitri Ver 2 Nitrite) were thoroughly dissolved by shaking and left for 10 minutes undisturbed as the reaction time. The outsides of the vials were thoroughly wiped before

insertion into the DR 3900 spectrophotometric instrument for reading. For the quality control the tests were read to ± 0.05 mg/L.

k. Colour

Colour was measured as true colour using spectrophotometric method – Platinum-Cobalt standard method (Method 8025) as adapted from HACH (2002). Prior to measurements, the leachate sample was filtered through filter crucibles of average pore size 40 μm and analysed at 120 colour, 455 nm using a DR 3900 HACH spectrophotometer. Platinum-cobalt (PtCo) are the units used for colour. A unit of colour is said to correspond to that produced by 1 mg platinum per litre in the form of the chloroplatinate ion (Aziz et al., 2004).

l. Temperature

Different mercury-in-glass thermometers were used to determine temperatures.

m. Dissolved Oxygen

Dissolved oxygen (DO) was measured using a YSI 550A probe as adapted from HACH (2002). Calibration was performed every time readings are conducted to ensure highest data accuracy. Before calibration the sensor was placed in its reading environment to read the barometric pressure. The meter was then allowed to read to +/-2% of 100% of air-saturated water for accuracy and quality control.

3.4 Results and Discussion: Leachate characterisation

The raw leachate samples were analysed and characterised at the University of Canterbury environmental laboratory on different dates. For accuracy and quality control purpose, the leachate was re-tested each time a new batch was received for the experiments. The samples were characterised for different physico-chemical parameters to estimate their initial contaminants. The results show that leachate samples contain very high ammonia concentrations, above the New Zealand discharge limits. The summary results of the leachate characteristics are presented in Table 3-1.

3.4.1 pH

pH is a very important parameter to the receiving environment because it influences chemical reactions. The pH values for the leachate as sampled on different dates were 7.78, 8.03, 7.82

and 7.95 respectively. These pH values indicate that the leachate has reached a stabilisation stage and also shows fairly constant pH values with little variations (Bhalla et al., 2012; Christensen et al., 2001b). Moreover, according to Christensen et al., (2001) the pH of leachates is generally around 4.5 to 9.0, and also the leachate pH changes with the age of the landfill. Young leachates generally have a pH of less than 6.5, while stabilised leachates have pH greater than 7.5 (Bhalla et al., 2012; Christensen et al., 2001b; Kurniawan, Lo, & Chan, 2006).

3.4.2 Ammonia nitrogen

The NH_3-N concentrations measured from the leachate were 2,180 mg/L, 2,040 mg/L, and 2,124 mg/L respectively. This leachate is very rich in ammonia and, moreover, ammonia is an inorganic component that causes serious concern in leachate (Johannessen, 1999). High concentrations of ammonia negatively impact the wastewater treatment processes and reduce the quality of the effluent, preventing it from meeting discharge standards (Poveda et al., 2016). Furthermore, an ammonia concentration higher than 100 mg/L is said to be very toxic to aquatic life (Aziz et al., 2004; Bashir et al., 2015). The ammonium ion (NH_4^+) has an oxygen demand as it changes to NO_3^- resulting in dissolved oxygen depletion from the surrounding water bodies. In addition, the concentration of typical domestic wastewater ranges from 35 m/L to 60 m/L. Therefore, this high NH_3-N concentration is a very important reason why landfill leachate requires treatment prior to discharge.

3.4.3 Chemical oxygen demand (COD)

The COD values measured from the leachate were 4,050 mg/L, 4,960 mg/L, 4,100 mg/L and 4,240 mg/L respectively. COD is a measure of the total oxygen needed to oxidise all the organic waste to inorganic products such as carbon dioxide and water (Bhalla et al., 2012). These measured COD values are considered very high compared with the standard limit. Moreover, such high concentrations could also affect the efficiency of biological treatment of the leachate (van Loosdrecht et al., 2016).

3.4.4 Nitrates

The nitrate values measured from the leachate were from 1.8 mg/L to 33 mg/L. The New Zealand discharge limit for nitrates is 11.0 mg/L, therefore the leachate is considered high in nitrates. However, the ratio of NO_3/NH_4 is very low and most of the nitrogen (N) is in the reduced NH_4 form.

3.4.5 Turbidity

Only samples from 27 June 2016 and 10 July 2016 were measured for turbidity. The turbidity values were measured to be 68.0 NTU and 58.4 NTU respectively. These values seem consistent with those found in some previous studies (Bhalla et al., 2012; Christensen et al., 2001b) For example, (Bhalla et al., 2012) analysed turbidity concentrations from three landfill sites at (Jainpur, Jamalpur and Noorpur) in Ludhiana (India) and their concentrations were 43 NTU, 79 NTU and 68 NTU, respectively.

3.4.6 Total suspended solids and total solids

The TS concentration of the samples were 8,620 mg/L, 10,180 mg/L, 9,860 mg/L and 9620 mg/L respectively, with an average of 9,470 mg/L. TS in the leachate consist of dissolved organic and inorganic salts (Bhalla et al., 2012; Christensen et al., 2001b). The suspended solids levels were found to be very low, with values of 57 mg/L, 57 mg/L, 137 mg/L and 97 mg/L respectively. Very high suspended solids impact on the receiving environment and also overload some of the treatment processes, hence affecting the effluent quality.

3.4.7 Colour

The leachate sample's colour was dark brown and the measured values were 8,580 Pt/Co, 8,920 Pt/Co and 8,790 Pt/Co respectively. Generally, stabilised leachate consists of high organic matter (humic and fulvic compounds) that bring about the dark brown colour of the leachate (Aziz et al., 2007). High colour values (6540 Pt/Co) were also recorded in previous studies such as by Aziz et al. (2007). Colour can adversely impact on the receiving water in many ways, such as:

- reducing photosynthesis processes
- reducing aesthetic values
- altering the ecosystem
- bathers stop swimming due to visibility issues in the waters.

3.4.8 Alkalinity

In this study alkalinity refers to the acid-neutralising capacity of the leachate sample and is measured as $CaCO_3$ concentration. The leachate alkalinity was measured to be 8,490 mg/L $CaCO_3$, 9,560 mg/L $CaCO_3$, 8,590 mg/L $CaCO_3$ and 8,860 mg/L $CaCO_3$ respectively.

Table 3-1: Canterbury Leachate Characteristics Sampled At Different Dates.

Sample	**Raw leachate**				**Typical Domestic wastewater**
Sample date	11/6/2015	5/5/2016	6/27/2016	7/10/2016	
Parameter					
pH	7.78	8.03	7.82	7.92	6.00–9.00
Turbidity, NTU	-	-	68.0	58.4	-
Total alkalinity, mg/L $CaCO_3$	8,495	9,565	8,590	8,855	100
Conductivity, mS/m	21.65	24.30	23.23	23.05	-
NH_3-N, mg/L	-	2,180	2,040	2,124	35
TKN, mg/L	1,960–2,038	2,390	2,185	2,306	
COD, mg/L	3,090–4,050	4,960	4,105	4,237	500
Colour, Pt/Co	-	8,580	8,920	8,790	
TSS, mg/L	55–57	57	137	97	300
TS, mg/L	8,621	10,184	-	9,615	800
NO_3 –N, mg/L	1.5–22.8	8.70–33	-	7–55	20
NO_2-, mg/L	-	-	-	-	-

3.5 Conclusion

The leachate samples were collected and analysed for different physico-chemical parameters to estimate their initial contaminants. The landfill leachate used for this research contains high concentrations of both organic and inorganic (NH_3-N) contaminants. This high ammonia nitrogen concentration is the reason why landfill leachate requires treatment prior to discharge. The measured pH values indicate that this leachate has reached stabilisation stage and also shows fairly constant pH values with little variation. Heavy metals were not measured at this stage. The high ammonia nitrogen concentration in leachate would require a more appropriate treatment method in order to reduce it to satisfactory levels, hence reducing cost of further treatment. This study investigated the possible options of treating ammonia in the next chapters.

CHAPTER 4. Coagulation–flocculation: Option 1

This study examined the use of both anhydrous ferric chloride and hexahydrate ferric chloride and also aluminium sulfate (alum) in removing ammonia nitrogen from landfill leachate through a coagulation–flocculation technique. The aim of this study was to investigate these coagulants in removing ammonia nitrogen and determine the best coagulant and optimum conditions. Jar test experiments were used to explore the best coagulant, effective dosage, effect of pH, mixing regimes and settling time. In addition, the effect of three commercial cationic polyelectrolytes in removing ammonia nitrogen from landfill leachate through coagulation–flocculation was also assessed.

4.1 Materials and method

4.1.1 Leachate sampling

As mentioned in Chapter 3 of this report leachate samples were collected from a landfill site situated in the Canterbury region in the South Island of New Zealand. The samples were collected at different times to minimise the possibility of sample biodegradation. The samples were stored at 4°C all the time until analysed. Refer to Chapter 3 of this report.

4.1.2 Coagulants and polyelectrolytes

The coagulants used in this study were anhydrous ferric chloride, hexahydrate ferric chloride and aluminium sulfate. These coagulants were purchased from Meck Corporation, New Zealand. Anhydrous ferric chloride and aluminium sulfate (alum) were supplied in the powdered form while hexahydrate ferric chloride was in the crystal form. The three cationic commercial polyelectrolytes used were Magnesol 598, Crystalfloc and Magnafloc LT7991. Magnesol 598 and Crystalfloc were supplied by Chemiplas Pty Ltd NZ whereas Magnafloc LT7991 was obtained from Ciba Speciality Chemical. The primary role of polyelectrolytes is to aid coagulants in flocs formation. The choice of polyelectrolytes used was through the recommendations from the suppliers and of course through literature review. A summary of polyelectrolyte properties is given in Table 4-1 and it shows that these polyelectrolytes are from the polyacrylamide family. According to some studies polyacrylamides are known to be a source of organic nitrogen (Kay-Shoemake et al., 1998). The polyacrylamide data sheets are presented in Appendix E.

Table 4-1: Polyelectrolytes Used with Optimum Dose of Hexahydrate Ferric Chloride.

Name of polyelectrolyte	**Chemical family**	**Charge**	**Molecular weight**	**Physical form**
Magnesol 598	Cationic polyacrylamide	cationic	High mol. wt.	liquid
Crystal floc	Polyacrylamide	cationic	-	liquid
Magnafloc LT 7991	Epichlorohydrina-mine	cationic	High mol. wt.	aqueous

4.2 Experimental methods

4.2.1 Coagulation–flocculation tests - jar tests

All the coagulation–flocculation studies were performed in a conventional jar test apparatus equipped with rectangular blade impellers (2.5 cm x 2.5 cm x 75 cm), each with six 500 mL or 1000 mL beakers. For every analysis, the landfill leachate samples were removed from the refrigerator for a period of approximately 2 to 3 hours and allowed to reach ambient temperature prior to testing. After 2 to 3 hours, the leachate sample temperature was measured and would range between 17ºC to 22ºC. Moreover, prior to analyses the samples were thoroughly agitated for resuspension of settled solids. The leachate sample volumes (500 or 1000 mL) were then transferred into the corresponding beakers of the jar test. The jar test experimental procedure involved three successive stages:

- The first stage was initial rapid mixing for 1 to 5 minutes at various velocities ranging from 60 to 100 revolutions per minute (rpm).
- The second stage was a slow mixing stage which lasted between 10 to 60 minutes at various speeds ranging from 20 to 60 rpm.
- The final stage of the coagulation–flocculation test was the settling period which lasted for at least 30 minutes.

The mixing speed was kept constant in all six containers by a gauge at the top centre of the device. The jar test set is shown in Figure 4-1. The jar test processes entailed adjusting the leachate sample pH levels where applicable. Where necessary pH adjustment was performed either using solutions of 1.0N HCl or 1.0N NaOH to reach the desired levels.

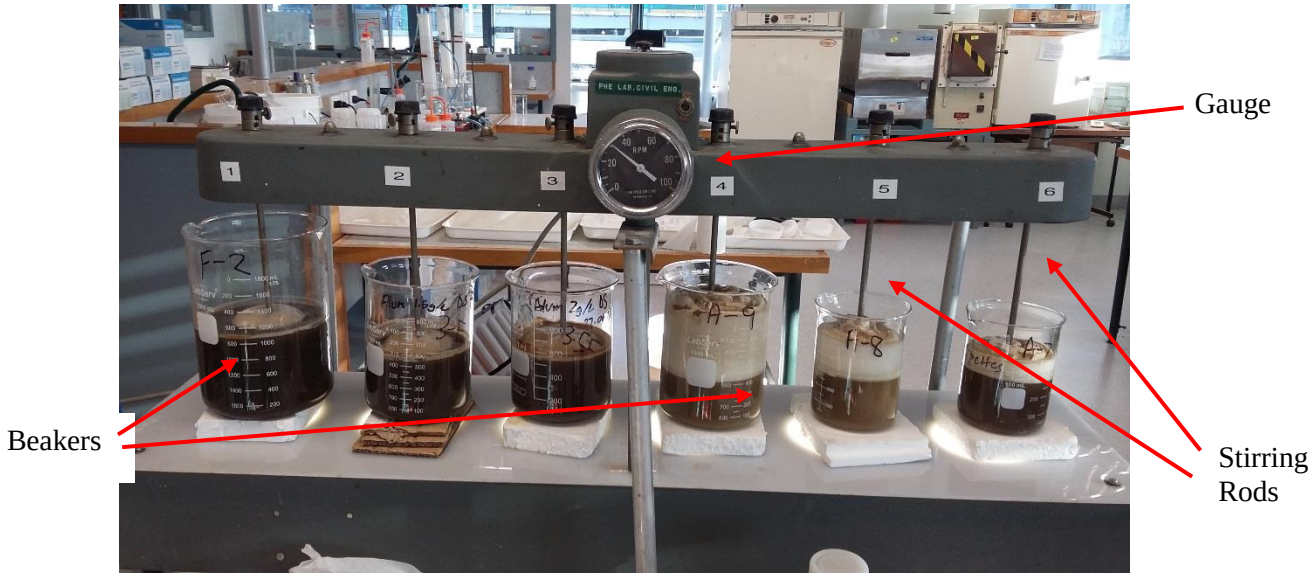


Figure 4-1: Coagulation–flocculation jar test apparatus.

In experiments using polyelectrolytes, these were added after the rapid mixing stage to correspond with the slow mixing stage. After the final stage (settling) of coagulation–flocculation, the 10 mL pipette was used to withdraw the supernatant from the beakers. Withdrawal of the supernatant was done at a point below the bottom of the suspended foam if any. Prior to supernatant analysis, the sludge volume at the bottom of the beakers was estimated and recorded. The supernatant was analysed for NH_3, COD, turbidity, SS, colour and for final pH where necessary. As mentioned in Chapter 3, the analysis for NH_3-N was conducted using the distillation and titration method using the Micro-Kjeldahl method 4500-N of the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005). All other parameters were analysed as explained in Chapter 3 of this report.

The amount of titrant used in the distillation and titration method was converted into the NH_3-N concentration using the Equation 21 of Chapter 3 (3.3.1c).

The removal efficiency of ammonia nitrogen, COD, turbidity, SS and colour was found using the following formula:

$$\% \text{ removal } = \frac{(C_i - C_f)}{C_i} X\ 100 \quad \textbf{(24)}$$

where:

C_i = initial concentrations of ammonia, COD, turbidity, SS and colour (mg/L)

C_f = initial concentrations of ammonia, COD, turbidity, SS and colour (mg/L)

4.2.2 Variables explored

The variables explored and optimised in this study were coagulant type and dosage, pH, polyelectrolytes addition, rapid and slow mixing regimes and settling time. Challenges were encountered in adjusting the pH below 7.0 and above 8.0 with the addition of HCl and NaOH. Rapid foaming occurred which made it difficult to adjust the pH to levels below 7.0 and above 8.0. However, where possible to mitigate this problem drops of antifoaming agent (amyl alcohol) was added as needed.

Figure 4-2 shows leachate pH adjustment apparatus and steps used in this study. Whereas, Figure 4-3 shows ammonia test apparatus and steps also used in this study.

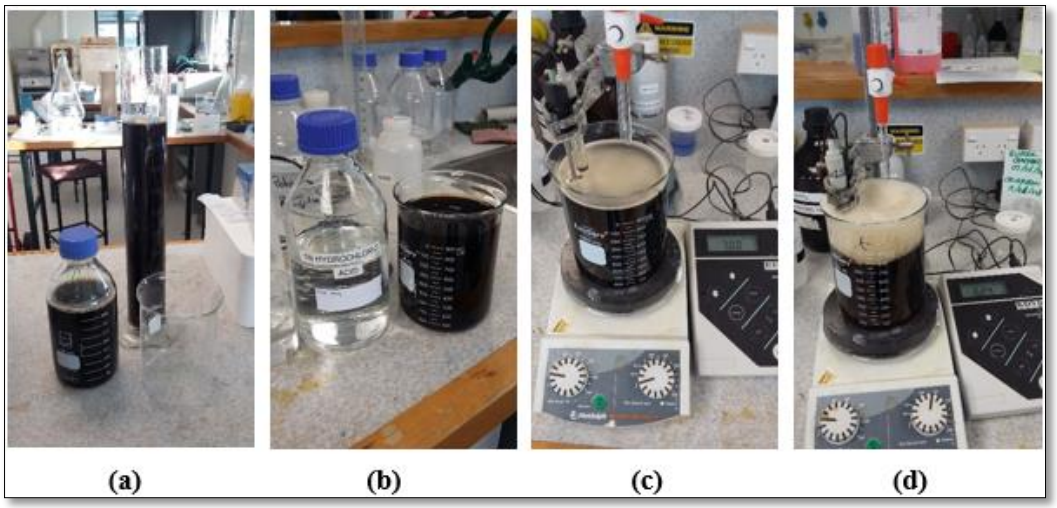


Figure 4-2: (a) & (b) Leachate sample preparation for pH adjustment. (c) Leachate sample adjustment to pH 7.0. (d) Leachate sample foaming as adjusted to pH 6.0.

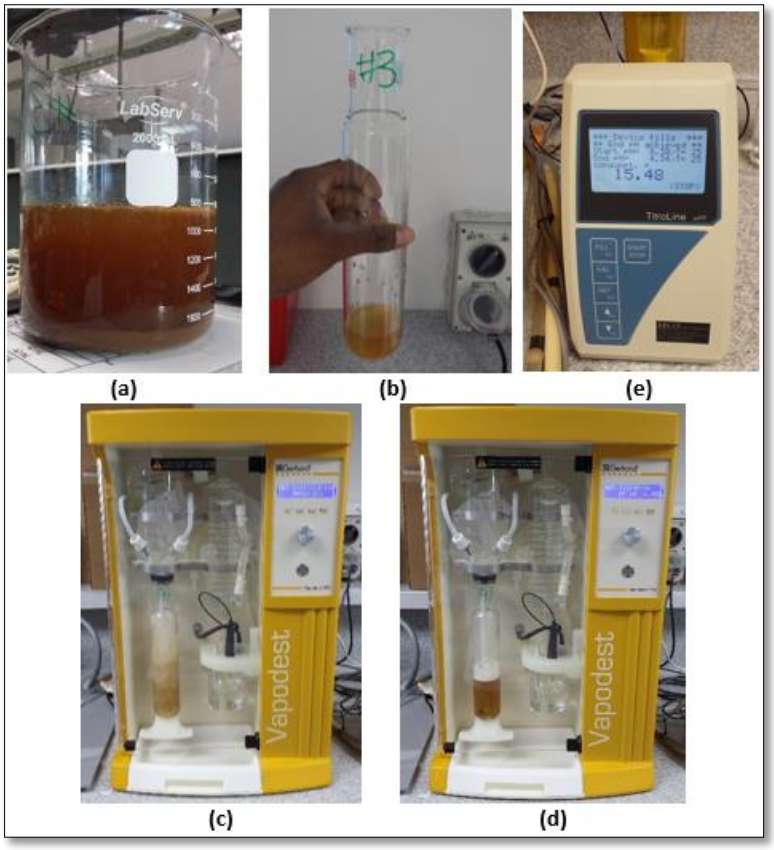


Figure 4-3: (a) Coagulated sample. (b) 20 mL of supernatant ready for analysis. (c & d) Distillation and titration stage using Vapodest 4s machine. (e) Titroline reading the amount of titrant used.

4.2.3 Re-producing results from previous studies

This study also attempted to reproduce the best coagulation–flocculation results from previous studies using anhydrous ferric chloride and alum. The raw leachate pH was adjusted to pH 7.0 and 5.0 with the addition of hydrochloric acid for experiments with anhydrous ferric chloride and alum respectively. This study kept every condition constant with anhydrous ferric chloride experiments except with rapid mixing speed as shown in Table 4-2. The jar test gear used in this study was limited to a maximum speed of 100 rpm. Challenges were encountered in adjusting the pH to 4.8 due to vigorous foaming. Therefore, this study could only adjust the raw leachate pH to pH 5.0. Table 4-2 shows the coagulation–flocculation schedule for reproducing the previous studies' results.

Table 4-2: Coagulation–Flocculation Schedule for Re-Producing Results of Previous Studies.

Study	**Coagulant**	**pH**	**Dosage** (mg/L)	**Mixing time** (minutes)	**Mixing speed** (rpm)	**Settling time** (minutes)	**Initial NH_3** (mg/L)
Rui et al. 2012	Ferric chloride	7	2,000	4	150	30	1,700
This Study	Ferric chloride	7	2,000	4	100	30	2,261
Rui et al. 2012	Ferric chloride	7	3,500	4	150	30	1,700
This Study	Ferric chloride	7	3,500	4	100	30	2,261
Syafalni et al. 2012	Alum (powder form) $Al_2(SO_4)_3.16H_2O$ (M = 630.39 g/mol)	4.8	10,000	3	150	30	2,040
This Study	Alum (powder form) $Al_2(SO_4)_3.18H_2O$ (M = 666.45 g/mol)	5	10,000	3	150	30	2,261

4.2.4 Visual test

During the jar test the following observations were made:

- foaming during pH adjustments
- foaming during coagulation test
- floc formation
- wet sludge volume
- settling time
- floating suspended solids
- colour and clarity of supernatant.

4.2.5 Wet sludge volume estimates

During the coagulation–flocculation treatment process, sludge is produced, which could be a concern. The suspended solids, together with the compounds formed by the coagulant, produce the sludge (Aguilar et al., 2002). The amount of sludge produced is an aspect to be considered in selecting the most effective coagulant for treatment (Aguilar et al., 2002). If a large amount of sludge is produced, it could create another potential problem, resulting in another treatment having to be employed, therefore proving very costly. However, the sludge formed during the coagulation–flocculation treatment process could be used to harvest or recover the coagulants employed in the treatment (Aguilar et al., 2002). Moreover, the sludge might be used in agricultural applications after adequate analysis and treatment. In this study, the wet sludge volume was estimated to compare the effectiveness of each coagulant. It was estimated from

the level of the sludge to the bottom of the beaker as shown in Figure 4-4. The estimation was also calculated as below:

$$\text{wet sludge volume (\%)} = \frac{B}{A} \text{ x } 100 \quad \textbf{(25)}$$

Where:

A = coagulated sample volume

B = sludge volume from the bottom of the beaker.

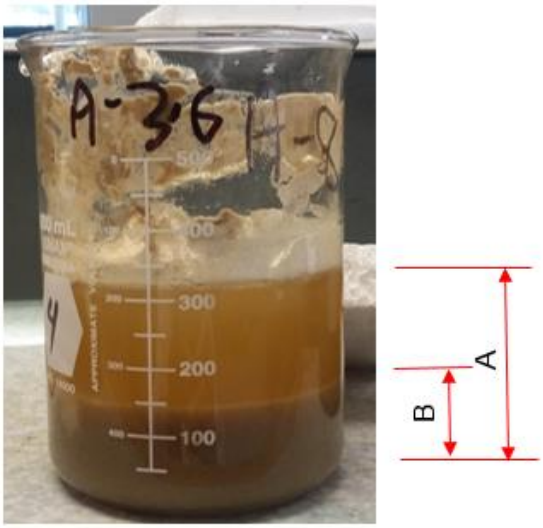


Figure 4-4: Estimating wet sludge volume after coagulation–flocculation with alum.

4.3 Results and discussion

4.3.1 Experiments re-producing results from previous studies

4.3.1.1 Anhydrous ferric chloride

To reproduce the results of Rui et al. (2012) as shown in Table 4-2, the experiments were performed with anhydrous ferric chloride at a constant raw leachate pH adjusted to pH 7.0. The raw leachate pH was adjusted prior to jar tests with 1.0N hydrochloric acid. For these experiments two coagulant dosages of 2,000 mg/L and 3,500 mg/L of anhydrous ferric chloride were analysed with an initial rapid mixing regime of 100 rpm for 4 minutes. The rapid mixing regimes were followed by a slow mixing regime of 30 rpm for 20 minutes. Thereafter, stirring was stopped and the formed flocs were allowed to settle for 30 minutes before withdrawing the supernatant for analysis. The results are presented in Table 4-3. As observed, the preliminary results conducted by this study obtained the highest NH_3-N removal of 36.5 % compared with 26 % obtained by Rui et al. (2012) with same $FeCl_3$ dosage (2,000 mg/L). Moreover, this study

obtained better COD results compared with those of Rui et al. (2012) at the same dosage. However, better colour removal was achieved by Rui et al. (2012). The removal of NH_3-N, the COD and colour were lower in this study (11%, 38% and 42% respectively) than the values of Rui et al. (2012) with a dosage of 3,500 mg/L. More information of these experiments is presented in Appendix F.

After the flocs had settled for at least 30 minutes, the wet sludge volume was estimated for each dose from the total treated leachate volume. The sludge volume production was 30% (2,000 mg/L) and 40% (3,500 mg/L) and increased with increasing $FeCl_3$ doses.

I believe that the difference in these results could possibly be attributed to but not limited to the following:

- The difference in the initial NH_3-N concentrations in each leachate. The initial NH_3-N concentrations used in this study were 30% higher than those analysed by Rui et al. (2012).
- The difference in the levels of other compounds in the leachate samples could be a factor.
- The temperature conditions during the experiments could have been different, so influencing the results.

However, they could be other factors such as analytical problems that could have possibly led to the difference in the results.

4.3.1.2 Aluminium sulfate

To reproduce the results of Syafalni et al. (2012) as shown in Table 4-2, the experiments were conducted with aluminium sulfate at a raw leachate pH adjusted to pH 5.0. In this experiment difficulties were encountered in adjusting the pH to 4.8 due to vigorous foaming. Therefore, this study could only adjust the raw leachate pH to pH 5.0. A higher alum dose of 10,000 mg/L was used with an initial rapid mixing regime of 100 rpm for 3 minutes. The slow mixing regime, settling and analyses were similar to that with $FeCl_3$. The results are presented in Table 4-3. It was observed that this high dose of alum achieved low removal results of NH_3-N and COD (25.3% and 46% respectively) compared with the results of Syafalni et al. (2012).

However, this study obtained high colour removal (75%) which was quite similar to that of Syafalni et al. (2012).

Similarly, the wet sludge volume was estimated for each dose from the total treated leachate volume after a settling period of at least 30 minutes. The sludge volume produced was 33% at an alum dose of 10, 000 mg/L. More information of these experiments is presented in Appendix F-1.

Once again, I believe the difference in these results could possibly be attributed to but not limited to the following:

- The difference in pH levels.
- The difference in the type of alum used which the study omitted in factoring the coagulant dose. Syafalni et al. (2012) used $Al_2(SO_4)_3.16H_2O$ and this study used alum with two extra molecules of H_2O, $[Al_2(SO_4)_3.18H_2O]$
- The difference in the level of other compounds in both leachate samples could be a factor.
- The temperature conditions during the experiments could have been different hence influencing the results.

Other factors such as analytical problems could have also possibly led to the difference in the results.

Table 4-3: Comparison of This Study's Results and Previous Studies' Results.

Study	**Coagulant**	**pH**	**Dosage** (mg/L)	**Mixing time** (minutes)	**Mixing speed** (rpm)	**Settling time** (minutes)	**Initial NH_3-N** mg/L)	**NH_3-N removal** (mg/L)	**COD removal** (mg/L)	**Colour removal** (mg/L)
Rui et al. (2012)	Ferric chloride ($FeCl_3$)	7.0	2,000	4	150	30	1,700	26.0	28.0	82.0
This study	Anhydrous ferric chloride ($FeCI_3$)	7.0	2,000	4	100	30	2,261	36.5	50.0	54.0
Rui et al. (2012)	Ferric ($FeCI_3$)	7.0	3,500	4	150	30	1,700	28.0	42.0	84.0
This study	Anhydrous ferric chloride	7.0	3,500	4	100	30	2,261	11.0	38.0	42.0
Syafalni et al. (2012)	Alum (powder form) $Al_2(SO_4)_3.16H_2O$ (M = 630.39 g/mol)	4.8	10,000	3	100	30	2,040	41.2	65.0	80.0
This study	Alum (powder form) $Al_2(SO_4)_3.18H_2O$ (M = 666.45 g/mol)	5.0	10,000	3	100	30	2,261	25.3	46.0	75.0

74

4.3.2 Coagulants explored

4.3.2.1 First batch experiments with anhydrous ferric chloride and alum

The first batch of anhydrous ferric chloride ($FeCl_3$) was investigated against alum at several doses ranging from 1,000 mg/L to 3,500 mg/L with $FeCl_3$ and 1,000 mg/L to 14,000 mg/L with alum. These experiments were performed at constant initial raw leachate pH of pH 7.0 adjusted using hydrochloric acid. The supernatant was then analysed for NH_3-N, COD, turbidity, SS and colour. The results are presented in Figure 4-5 to Figure 4-9. As shown in Figure 4-5, the highest NH_3-N (36%) removal was obtained with anhydrous ferric chloride at a dose of 2,000 mg/L. The highest NH_3-N removal achieved by alum was 14.5% at a high dose of 6,000 mg/L. The COD reductions were high with anhydrous ferric chloride, achieving 50.7% at a dose of 2,000 mg/L as shown in Figure 4-6, while COD reductions with alum increased with increasing alum dosage, achieving levels of 36% at a dose of 14,000 mg/L. Anhydrous ferric chloride used exhibited an increase in turbidity concentrations from the raw leachate turbidity (68.0 NTU) with increasing coagulant dosage (Figure 4-7). However, turbidity removal was observed at doses of 3,000 mg/L and 3,500 mg/L achieving removals of 6.5% and 31% respectively. In contrast, alum did not show any turbidity removal with increasing dosage, achieving the highest turbidity concentration increase of 700% at a dose of 7,000 mg/L.

As shown in Figure 4-8, again anhydrous ferric chloride achieved the highest colour removal of 76.7% at a high dose of 3,500 mg/L, while alum exhibited an increase in colour removal with increasing alum dosage, achieving 88.1% at a high dose of 14,000 mg/L. Only TSS were analysed with ferric chloride supernatant, and an increase in TSS concentrations was observed with increasing anhydrous ferric chloride dosage, as shown in Figure 4-9.

From these results, anhydrous ferric chloride proved more effective than alum in treating landfill leachate at pH 7.0. Most of this study's results agree with the results reported by Rui et al. (2012) except for colour and suspended solids. Rui et al. (2012) achieved colour removal above 80% with a ferric chloride dose of 2,000 mg/L, while this study observed 66% with the same dose. In addition, Rui et al. (2012) achieved colour removal of 40% with an alum dose of 2,000 mg/L, while this study observed 11% with the same dose. Generally, all the contaminants analysed achieved high percentages reduction with anhydrous ferric chloride at lower doses as compared to alum. Moreover, other studies by Amokrane, Comel, and Veroni (1997) and Aziz et al. (2007) found ferric chloride to be an effective coagulant in treating

landfill leachate. Amokrane et al. (1997) observed 94% and 87% of turbidity removal from landfill leachate with ferric chloride and alum respectively. Whereas, Aziz et al. (2007) achieved removals of 99% SS, 96.5% colour and 44.7% COD with ferric chloride while with alum they witnessed 70.4% SS, 54.9% colour and 26.9% COD removals. In view of all these treatment results, ferric chloride was chosen for this study to be a better coagulant than alum in treatment of this landfill leachate. Raw data for these experiments are presented in Appendix F.

a) Ammonia nitrogen results

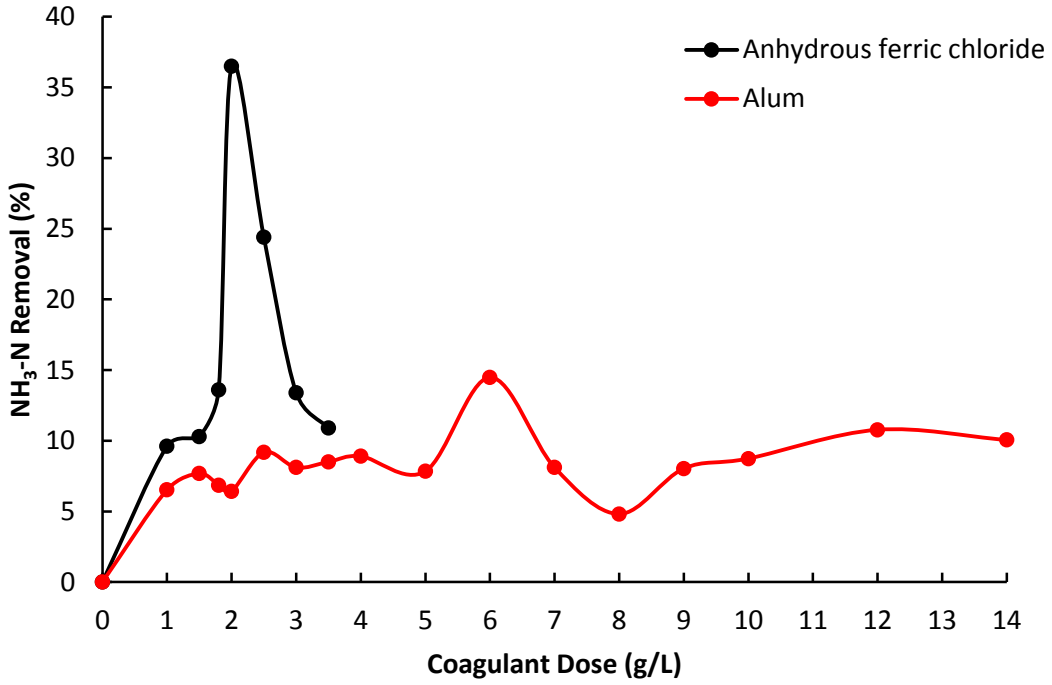


Figure 4-5: Effect of coagulant type and dosage on the removal of NH_3-N at a pH 7.0.

b) COD results

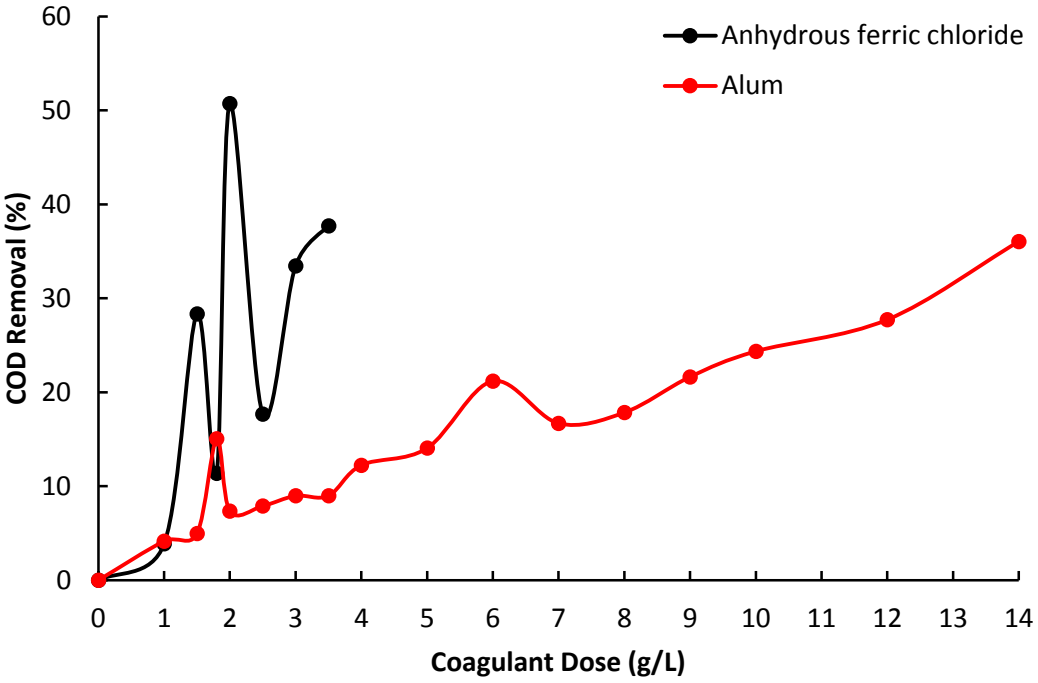


Figure 4-6: Effect of coagulant type and dosage on COD removal at a pH 7.

c) Turbidity results

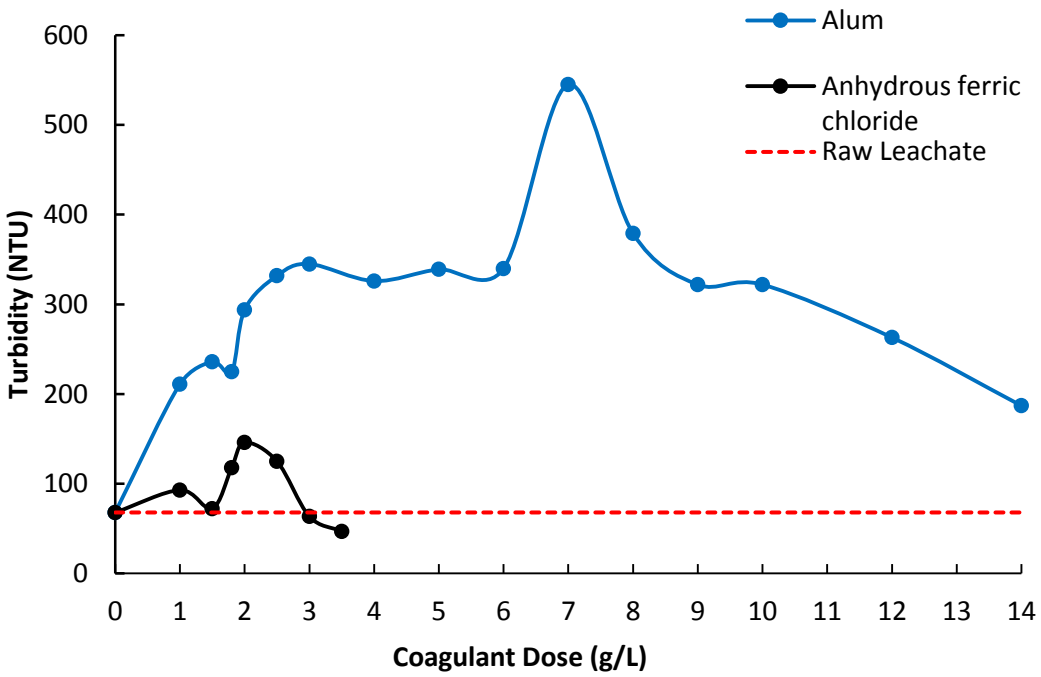


Figure 4-7: Effect of coagulant type and dosage on turbidity at a pH 7.0.

d) Colour results

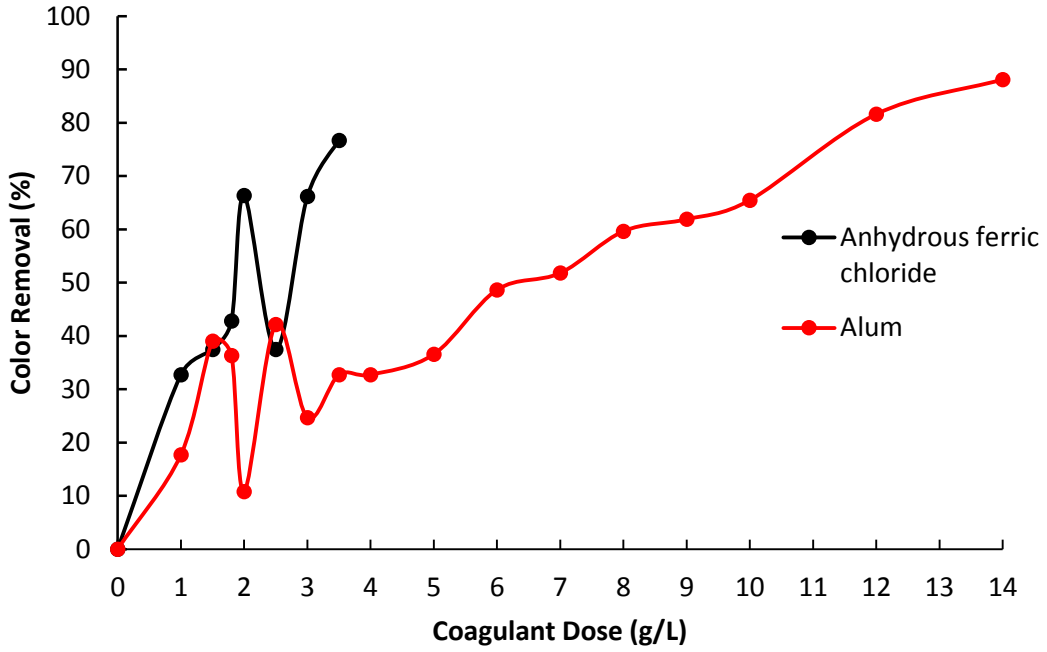


Figure 4-8: Effect of coagulant type and dosage on colour removal at a pH of 7.0.

e) TSS results

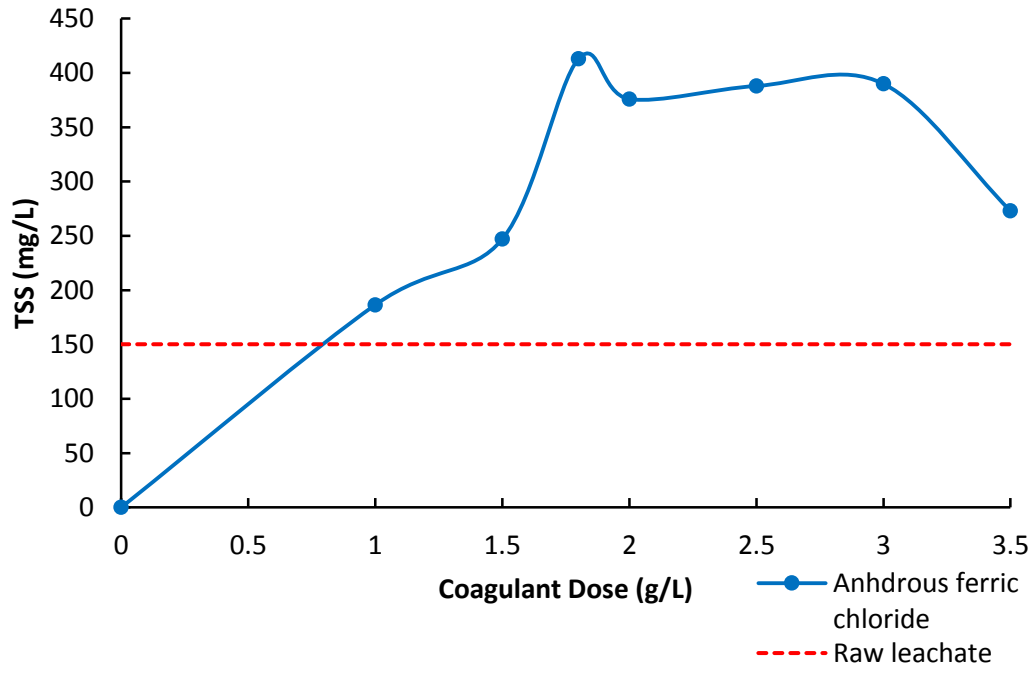


Figure 4-9: Effect of coagulant type and dosage on SS concentrations at pH 7.0.

f) Wet sludge volume

The sludge is produced from the suspended solids and the compounds formed during the coagulation (Aguilar et al., 2002). The sludge characteristics depend on the treatment conditions and the coagulant used. As shown in Figure 4-10, anhydrous ferric chloride produced more sludge volume at low coagulant doses. The sludge was estimated to be between 20% and 40% of the total treated leachate volume across the coagulant dosage. A higher sludge volume of 40% was observed at a dose of 3,500 mg/L, while less sludge was obtained with 1,000 mg/L. Less sludge production was observed with alum at lower doses. Both coagulants produced an increase in sludge production with increasing coagulant doses. Generally, alum exhibited better performance in sludge production than anhydrous ferric chloride.

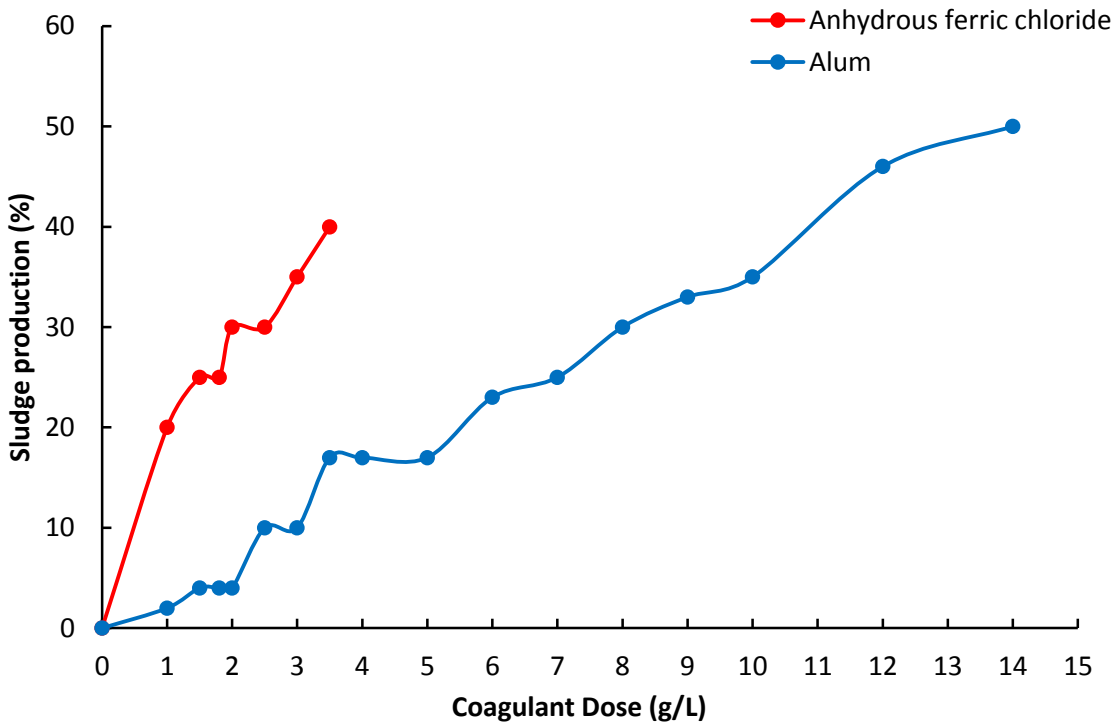


Figure 4-10: Wet sludge production with anhydrous ferric chloride and alum at pH 7.0.

4.3.2.2 Second batch experiments with anhydrous ferric chloride only

The second batch experiments were conducted at a later stage with only anhydrous ferric chloride at several doses ranging from 1,000 mg/L to 5,000 mg/L. These experiments were conducted in order to confirm the first batch results. The supernatant was analysed for NH_3-N, COD and turbidity reductions and the results are presented in Figure 4-11 to Figure 4-12. As

shown in Figure 4-11, these experiments with anhydrous ferric chloride achieved 20.4% of NH_3-N removal at a dose of 2,000 mg/L, while the first batch (anhydrous ferric chloride) results achieved 36.5% with the same dose (2,000 mg/L). Moreover, the COD reductions observed by these experiments was 28.5% at a dose of 2,000 mg/L while the highest (32.3%) was achieved at a dose of 5,000 mg/L. In contrast, the first batch (anhydrous ferric chloride) results observed 50.7% of COD reduction at a similar dose of 2,000 mg/L. Moreover, these experiments showed an increase in turbidity concentrations from the raw leachate turbidity (68.0 NTU) with increasing coagulant dosage (Figure 4-12). Very low (16.2%) turbidity removal was observed at a doses of 5,000 mg/L.

Generally, the second batch experiments observed low NH_3-N and COD reductions as compared to the first batch conducted with anhydrous ferric chloride. However, these experiments (second batch) still achieved similar COD and NH_3-N results obtained by Rui et al. (2012) with ferric chloride at a dose of 2,000 mg/L. Rui et al. (2012) obtained 28% and 26% of COD and NH_3-N reductions respectively while these experiments observed 28.5% and 20.4% of COD and NH_3-N reductions respectively.

Therefore, these results still indicate anhydrous ferric chloride as a more effective coagulant than alum in treatment of this landfill leachate. Raw data for these experiments are presented in Appendix G.

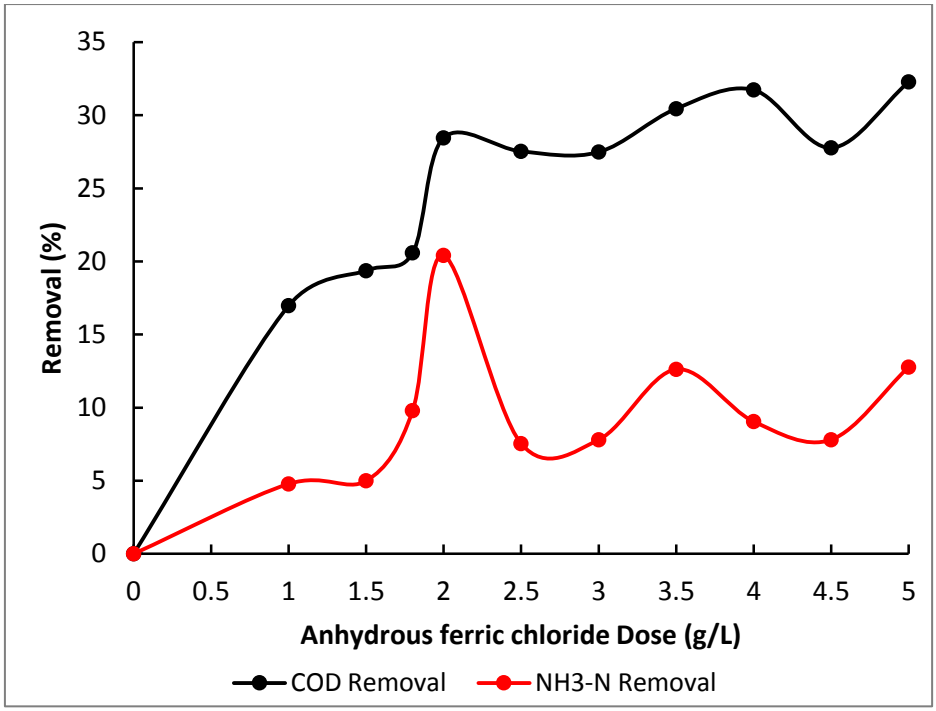


Figure 4-11: Effect of anhydrous ferric chloride dose on the removal of NH_3-N and COD at pH 7.0 before and after the coagulant addition.

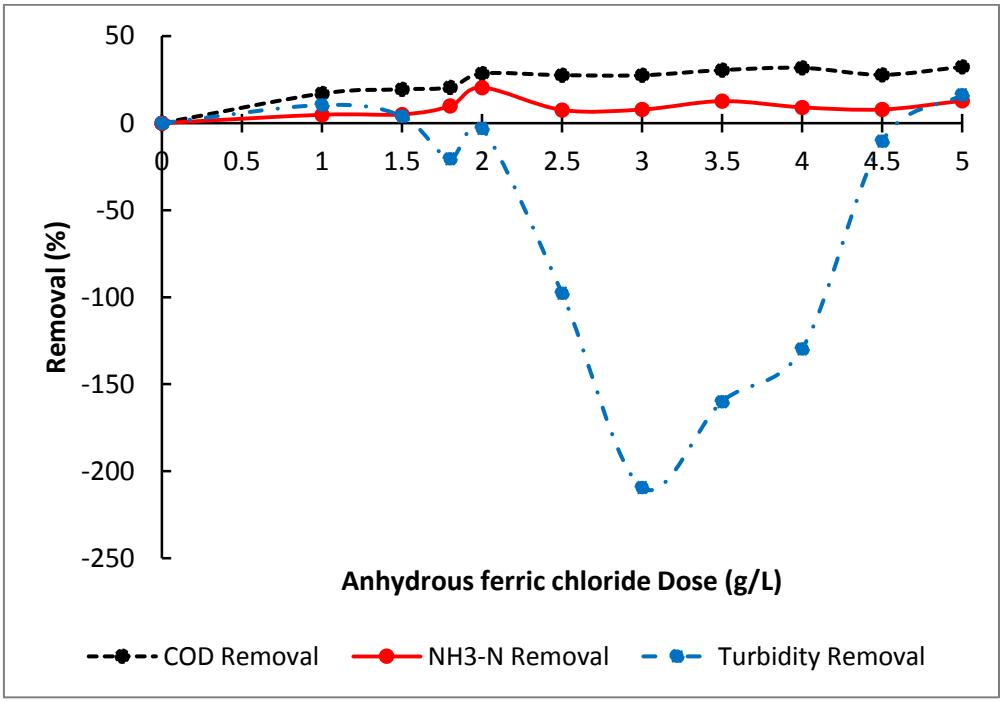


Figure 4-12: Effect of anhydrous ferric chloride dose on the removal of turbidity, NH_3-N and COD at pH 7.0 before and after the coagulant addition.

a. Wet sludge production

The wet sludge volume produced by these experiments was estimated to be between 15% and 40% of the total treated leachate volume across the coagulant dosage range (Figure 4-13). As shown Figure 4-13, the sludge production increased with increasing anhydrous ferric chloride dose. The sludge production followed the NH_3-N removal pattern, which indicates a correlation between sludge production and NH_3-N removal. As shown in the graph below, an increase in sludge production indicates an increase in NH_3-N removal. The doses between 1,000 mg/L and 2,500 mg/L produced less than 20% of wet sludge volume while doses from 3,000 mg/L to 5,000 mg/L produced 30% to 35% of wet sludge volume.

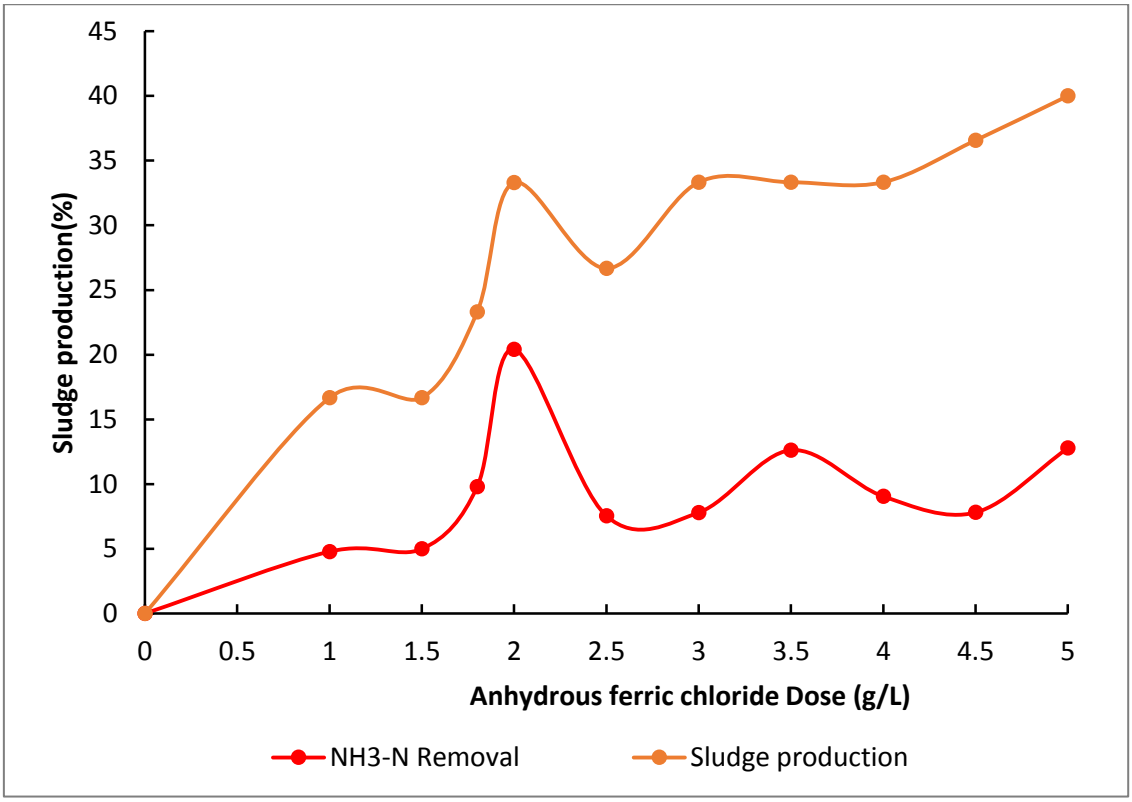


Figure 4-13: Wet sludge production at various anhydrous ferric chloride dose at pH 7.0

4.3.2.3 Possible cause of difference in results between first and second batch experiments.

The physical method of sludge generation was also used to analyse for the possible cause of the difference in the results of first batch and second batch experiments with anhydrous ferric chlorides. These sludge generation results are presented in Figure 4-14. According to Figure 4-14, the sludge generation from the two batches was very minimal however, could still be one of the possible cause of the difference in the treatment results (ammonia nitrogen and COD

removal results). The second batch experiments with anhydrous ferric chloride showed more sludge production at a dose of 2,000 mg/L than the first batch experiments with anhydrous ferric chloride. As mentioned elsewhere, sludge produced could possible result in NH_4^+ ions attaching to the metal salts precipitates during coagulation–flocculation resulting in ammonia nitrogen removal (Aguilar et al., 2002). Therefore, more sludge produced could possibly also assist in removal of ammonia nitrogen. However, this theory is challenged by the results observed at a dose of 2,000 mg/L of the both batches experiments with anhydrous ferric chloride.

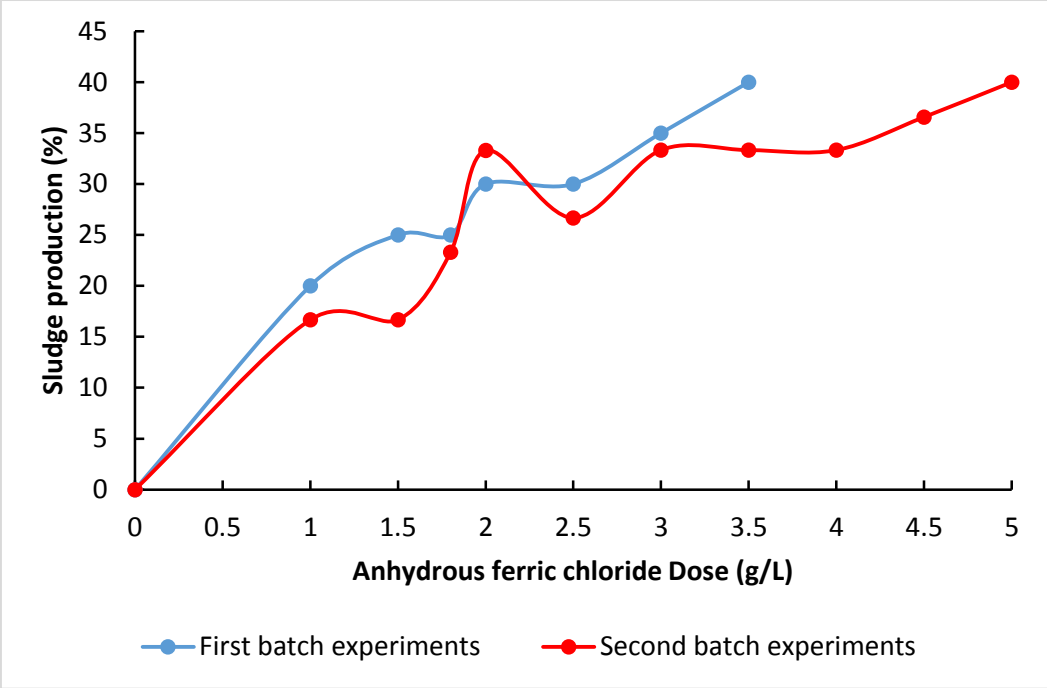


Figure 4-14: Wet sludge production with first batch and second batch experiments.

Moreover, there could be other reasons that led to the difference in the results of first batch and second batch experiments with anhydrous ferric chlorides used. Such as analytical problems that could be caused by the machinery used just to name a few. However, more in-depth analyses are needed to determine the possible cause.

4.3.3 Experiments with hexahydrate ferric chloride

Due to the problem with the availability of anhydrous ferric chloride from the suppliers at the time of the study, hexahydrate ferric chloride ($FeCl_3.6H_2O$) was used in this study for determining optimum dosage and optimisation. Experiments were conducted by duplicating

the dosages used in achieving high NH_3-N removal with anhydrous ferric chloride. Doses of anhydrous ferric chloride (1,800 mg/L, 2,000 mg/L and 2,500 mg/L) were multiplied by a factor of 1.67 to take care of the six water molecules ($FeCl_3.6H_2O$) present in hexahydrate ferric chloride, to produce the same mass of anhydrous ferric chloride used in the first batch experiments. These experiments were performed at a constant initial raw leachate pH of pH 7.0, adjusted using hydrochloride acid. The supernatant was then analysed for NH_3-N, COD and turbidity. The multiplication factor was calculated using the following equation;

$$\text{Factor} = \frac{\text{Molecular mass of hexahydrate ferric chloride}}{Molecular\ mass\ of\ anhydrous\ ferric\ chloride} \quad \textbf{(26)}$$

$$= \frac{270.30 \text{ g/mol}}{162.21 \text{ g/mol}}$$

$$= 1.67$$

where:

- molecular mass of anhydrous ferric chloride, $FeCl_3$, M = 162.21 g/mol
- molecular mass of hexahydrate ferric chloride $FeCl_3.6H_2O$, M = 270.30 g/mol

The results are presented in Figure 4-15. In this case, it was found that the experiments conducted using hexahydrate ferric chloride could not reproduce the initial results achieved using anhydrous ferric chloride (first batch experiments). As shown in Figure 4-15, the highest NH_3-N removal observed was 9.24% at the optimum dose of 3,000 mg/L. Aguilar et al. (2002) found similar NH_3-N results (<10%) with ferric chloride using the coagulation–flocculation method to treat an effluent from a slaughterhouse. The highest COD reductions achieved with hexahydrate ferric chloride was 26.24% at a high dose of 5,000 mg/L. Moreover, hexahydrate ferric chloride showed an increase in turbidity concentrations in the supernatant with increasing coagulant dose. Raw data for these experiments is presented in Appendix H.

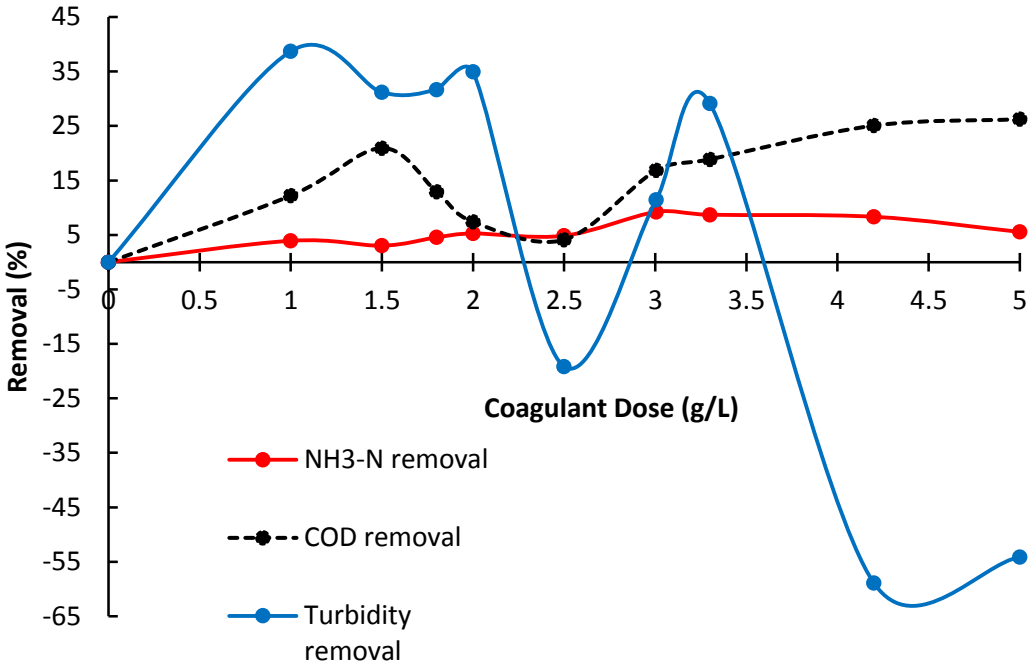


Figure 4-15: Effect of hexahydrate ferric chloride on the removal of NH_3-N, COD and turbidity at pH 7.0.

a) Wet sludge volume

The wet sludge volume produced by these experiments was estimated to be between 2% and 35% of the total treated leachate volume across the coagulant dose range. The doses between 1,000 mg/L and 2,500 mg/L produced less than 20% of wet sludge volume while doses from 3,000 mg/L to 5,000 mg/L produced 30%–35% of wet sludge volume. More information on these experiments is presented in Figure 4-16 and Appendix H.

b) Possible difference

As shown in Figure 4-16, the sludge generation between the anhydrous ferric chlorides and hexahydrate ferric chloride was different and that could be one of the cause of the difference in the treatment results (ammonia nitrogen, COD and turbidity removal results). Generally, hexahydrate ferric chloride produced less sludge compared to anhydrous ferric chloride, which might have contributed to lower ammonia nitrogen reductions. Aguilar et al. (2002) reported on possible ways ammonia nitrogen could be removed from wastewater through a coagulation–flocculation technique. These include ammonium ions adsorbing onto the hydrolysed products produced by metal ions during coagulation–flocculation, hence resulting in ammonia nitrogen removal. That study also highlighted NH_4^+ ions being removed as they attach to the surface of the negatively charged colloidal particles through electrostatic attraction. Aguilar et al. (2002)

further explained that NH_4^+ ions sometimes attach to metal salt precipitates during coagulation–flocculation, resulting in ammonia nitrogen removal.

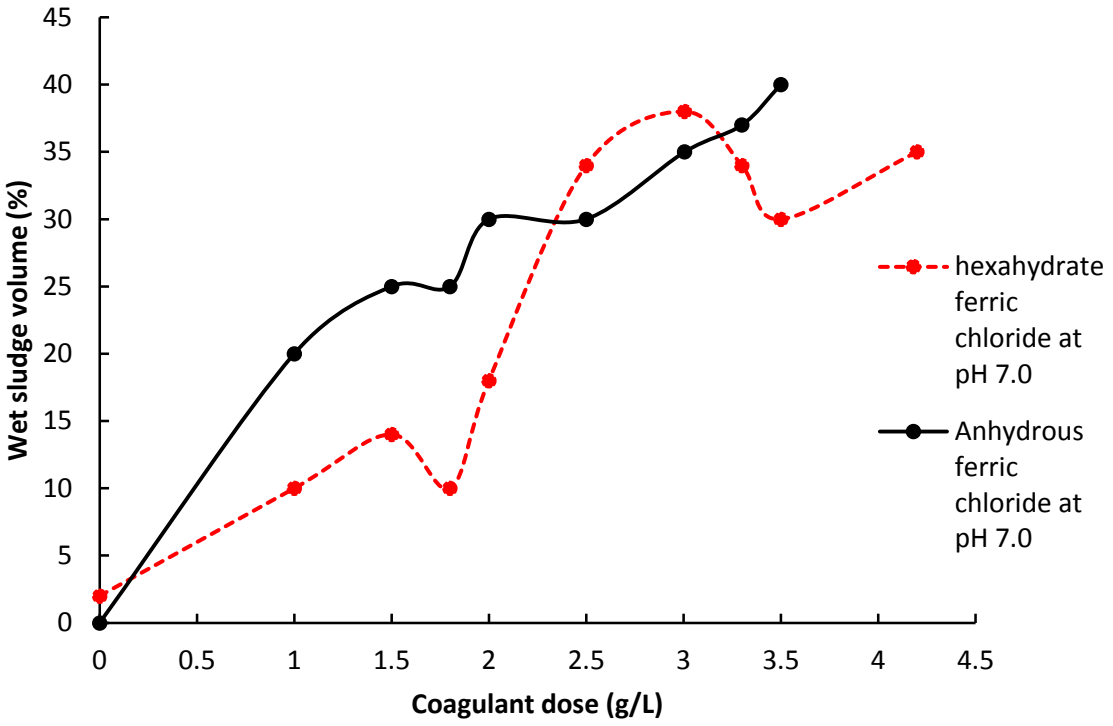


Figure 4-16: Wet sludge volume production of hexahydrate ferric chloride (adjusted to dry weight) and anhydrous ferric chloride.

Moreover, there could be other reasons that led to the difference in the results of anhydrous ferric chlorides experiments and hexahydrate ferric chloride experiments. Such as analytical problems that could be caused by the machinery used just to name a few. However, more in-depth analyses are needed to determine the possible cause.

4.3.4 Other variables investigated

4.3.4.1 Effect of adding polyelectrolytes to coagulants (hexahydrate ferric chloride)

The addition of polyelectrolytes to the coagulant (hexahydrate ferric chloride) was also investigated. These experiments were conducted by interacting hexahydrate ferric chloride with cationic commercial polyelectrolytes such as Magnesol 598, Crystalfloc and Magnafloc LT7991. As mentioned elsewhere in this study, the primary role of polyelectrolytes is to aid coagulants in floc formation, hence facilitating the removal of pollutants in wastewater or

leachate. The polyelectrolytes were used at 0.1% to 2.5% of the leachate sample (1 to 25 mL/L during flocculation stage), whereas the hexahydrate ferric chloride dose was kept constant at a dose of 3,000 mg/L.

As shown in Figure 4-17, the addition of polyelectrolytes slightly reduced the NH_3-N removal with increasing polyelectrolytes doses. The condition to this could be because the polyelectrolytes used were from the polyacrylamide family. According to some studies polyacrylamides are known to be a source of organic nitrogen (Kay-Shoemake et al., 1998). With this condition, the results are expected to show a linear decline in NH_3-N removal such as the results of hexahydrate ferric chloride with Crystalfloc. However, a different pattern (non-linear decline) is shown by hexahydrate ferric chloride with Magnesol 598 and hexahydrate ferric chloride with Magnafloc LT7991. Some other things (analytical problems) could have happened that led to this difference in patterns. However, this study did not investigate more on this. Summary results data of these experiments is presented in Appendix I.

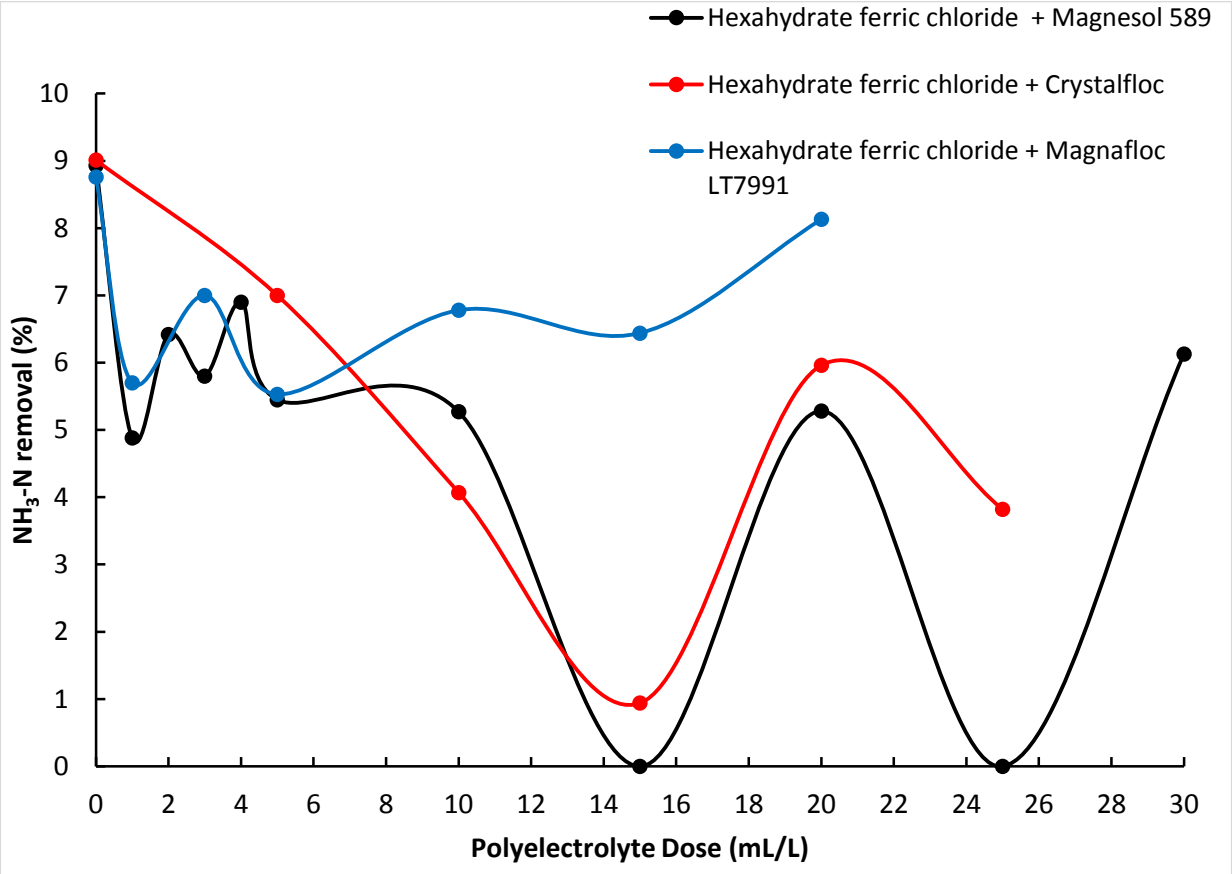


Figure 4-17: Effect of polyelectrolyte addition on NH_3-N removal at optimum hexahydrate ferric chloride dose (3.0 g/L).

A different pattern was observed with COD removal only with the addition of Magnesol 589, as indicated in Figure 4-18. An increase in COD reduction was observed with increasing ferric chloride dose from 1,000 mg/L to 5,000 mg/L, achieving a maximum of 45% at 5,000 mg/L. Thereafter, the COD reductions decreased. From the results obtained with addition of Crystalfloc and Magnafloc LT7991, a decline in COD reductions was observed with increasing polyelectrolyte dosages. According to these results, it may be stated that the polyelectrolytes used in this study do not improve the removal results of NH_3-N and COD. Very low COD reductions (1% to 40%) were also observed by Tsatsi et al. (2003) when adding flocculants to ferric chloride in treating sanitary landfill leachate through coagulation–flocculation.

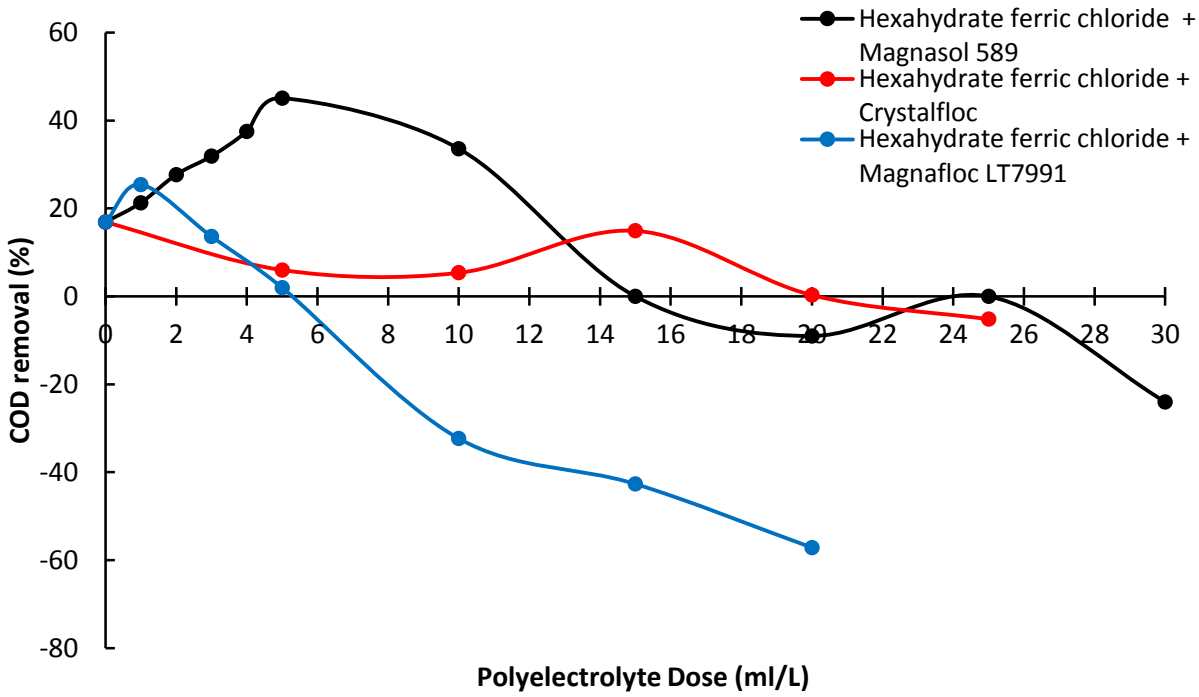


Figure 4-18: Effect of polyelectrolyte addition on COD removal at optimum hexahydrate ferric chloride dose (3,000 mg/L).

Turbidity reduction results are shown in Figure 4-19. All the experiments with results above the raw leachate turbidity concentrations (red) indicate no turbidity reductions. Gel-like flocs that do not settle were observed with the addition of Crystalfloc to hexahydrate ferric chloride. This increased the turbidity concentration of the supernatant, as indicated by Figure 50. Experiments with hexahydrate ferric chloride and Magnesol 586 obtained high turbidity reductions with increasing polyelectrolyte dose. The turbidity reductions obtained were 90%, 87%, 71% and 69% at doses of 20 ml/L, 5.0 ml/L, 10 ml/L and 4.0 ml/L respectively. Experiments with Magnafloc LT7991 yielded variable results. Reduction of 27%, 57% and

67% were observed at polyelectrolyte doses of 3.0 ml/L, 5.0 ml/L and 15 ml/L respectively. Aziz et al. (2007) observed that flocculants did not improve removal of COD, turbidity or colour after adding them to coagulants when treating young leachates. This study agrees with their statement with regard to NH_3-N and COD removal. However, good reductions of turbidity were observed in this study. Summary results data of these experiments is presented in Appendix I.

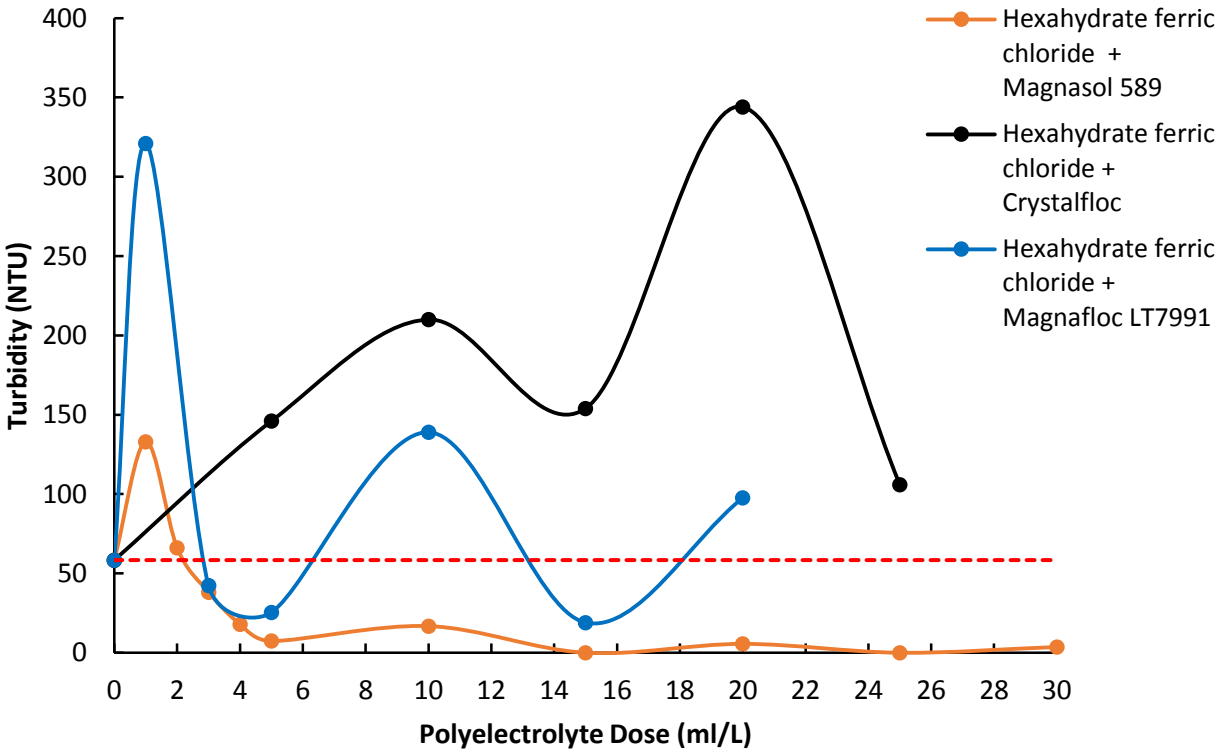


Figure 4-19: Effect of polyelectrolyte addition on turbidity concentrations at optimum hexahydrate ferric chloride dose (3,000 mg/L).

c) Wet sludge volume

As mentioned earlier, gel-like flocs that did not settle were observed with addition of Crystalfloc to hexahydrate ferric chloride; therefore sludge measurements could not be performed. The wet sludge production estimates are shown in Figure 4-20. Experiments with Magnesol 589 addition to hexahydrate ferric chloride showed an increase in wet sludge production with increasing polyelectrolyte doses. A maximum of 64% of wet sludge production was observed with high polyelectrolyte dose (30 ml/L). However, experiments with the addition of Magnafloc LT7991 obtained a tremendous reduction in wet sludge production with increasing polyelectrolyte doses. As shown in Figure 4-20, Magnafloc LT7991 reduced the sludge production from 16% to 3% with doses of 10 ml/L to 30 ml/L. Coagulation–flocculation

experiments by Amokrane et al. (1997) observed that cationic polymers were not effective in reducing sludge production in landfill leachates. The results with Magnesol 589 produced by this study agree with those of Amokrane et al. (1997). However, experiments with addition of Magnafloc LT7991 proved to be effective in reducing sludge production.

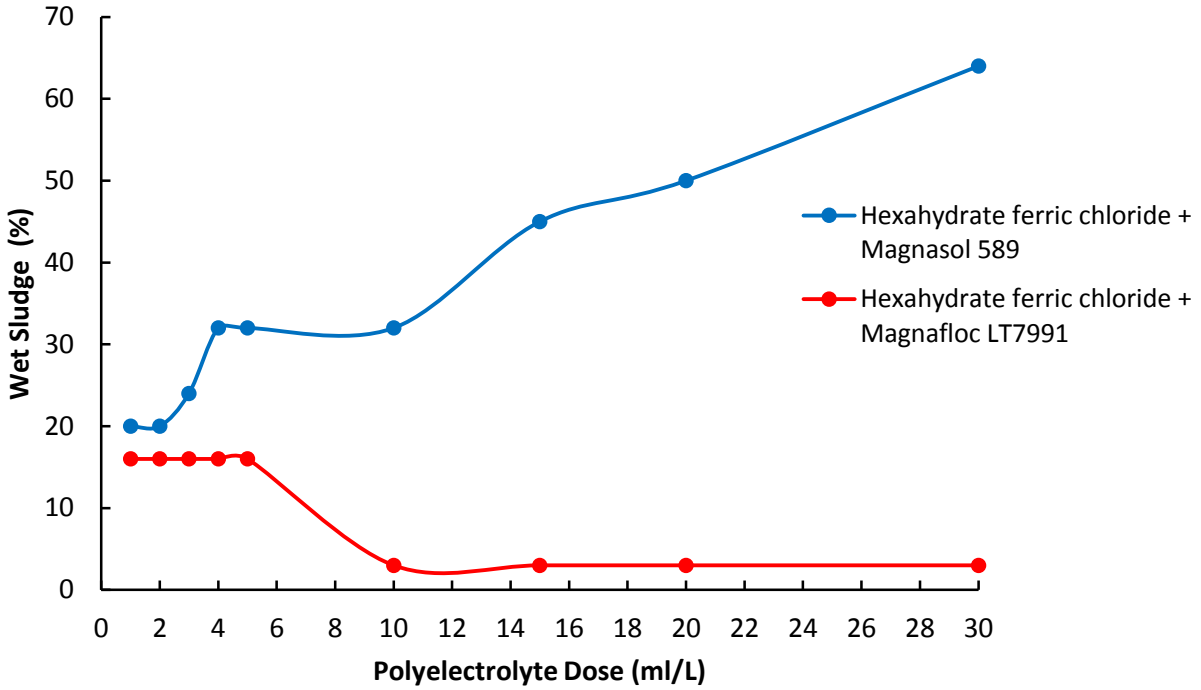


Figure 4-20: Effect of polyelectrolyte on wet sludge production at optimum hexahydrate ferric chloride dose (3,000 mg/L).

4.3.4.2 Experiments with alum as a coagulant at different pH

According to other studies alum yields the best treatment results at an optimal pH between 6.0 and 10.0 (Amokrane et al., 1997; Aziz et al., 2007; Marañón et al., 2010; Tsatsi et al., 2003). In this study both pH and alum dosages were varied. The pH was adjusted to pH 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0 using sodium hydroxide. The alum dosages were varied from 1,000 mg/L to 11,000 mg/L. The supernatant was tested for NH_3-N, COD and turbidity for each pH level. The wet sludge volume generation was also measured to monitor the influence of pH and alum doses on its production. The results are presented in Figure 4-21.

As shown in Figure 4-21, very significant NH_3-N removal was observed before the coagulation–flocculation process, after the pH was adjusted from pH 9.0 to pH 10.0. A minimum of 8.7% was recorded at pH 9.0 while pH 10 recorded a high of 39.6%. These NH_3-N reductions are likely to be because of a process called volatilisation where NH_4^+ escapes into

air as gaseous NH_3 (Terry, Nelson, Sommers, & Meyer, 1978). Terry et al. (1978) further explains that at pH 9.0 there is an increase of OH^- concentrations in the solution that cause the shift of NH_4^+ ions and NH_3 dynamic equilibrium, hence favouring the loss of NH_4^+ by volatilisation (as gaseous NH_3). However, a decrease in NH_3-N removal was observed at pH 10 with an increase in alum doses.

A significant increase in NH_3-N removal with increasing alum dose was observed at pH 9, achieving a maximum of 17.4% at a dose of 10,000 mg/L. This could be due to re-dispersion of coagulated particles that takes place with high pH values, hence NH_3-N removal through sweep flocculation. Thereafter a decrease was observed with further increases in alum dose. The two neutral pH levels (7.0 and 8.0) showed a fluctuating, low NH_3-N removal with increasing alum doses. They both achieved their maximum NH_3-N removals (10.7% and 11.9% respectively) at high doses of 11,000 mg/L. Overall, alum at neutral pH levels performed similarly to hexahydrate ferric chloride at low dosages (<10% NH_3-N removal).

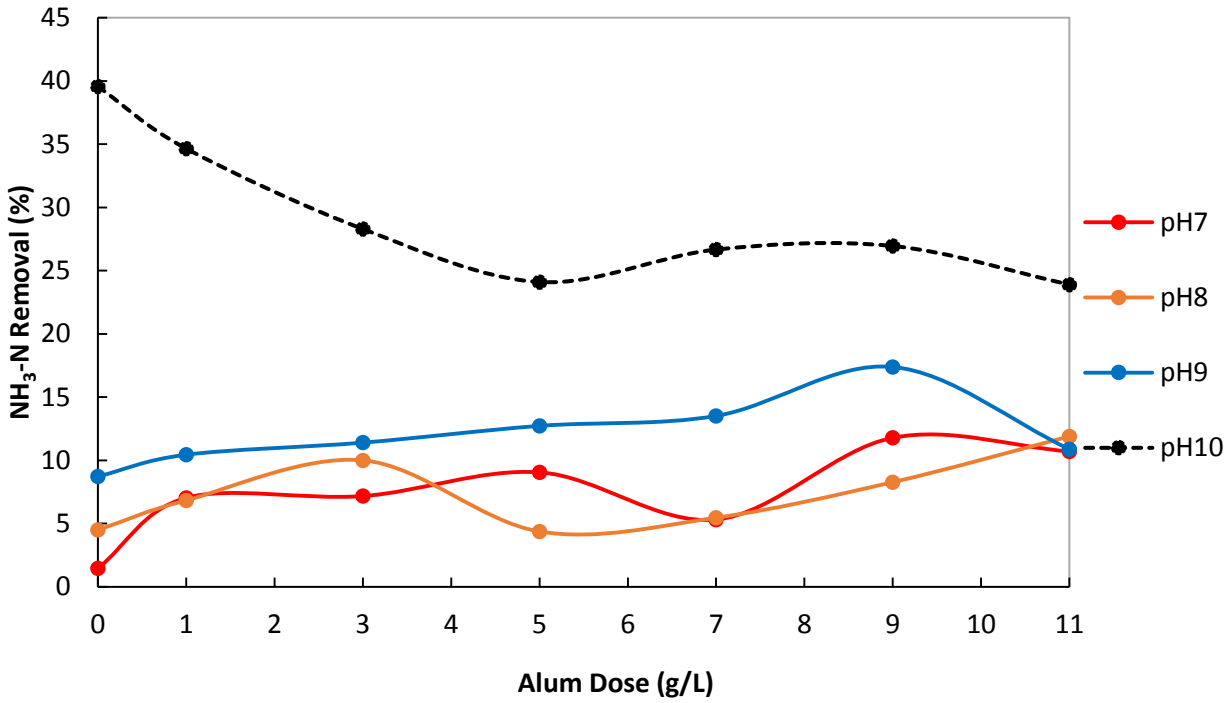


Figure 4-21: Effect of pH on NH_3-N removal at various alum dosages.

As shown in Figure 4-22, significant COD reductions were observed at pH 7.0 and pH 8.0 with increasing alum dose. A maximum reduction of 37.3% was achieved at pH 7.0 at an alum dose of 11,000 mg/L, while at pH 8.0, a maximum of 34.8% at an alum dose of 11,000 mg/L was

observed. Experiments at pH 9.0 seemed to yield fluctuating COD results, achieving high COD reduction of 30% at a coagulant dose of 5,000 mg/L. Not much change in COD reduction was observed at pH 10.0 with increasing coagulant dose. This pattern is likely to have been prompted by volatilisation process. Overall, hexahydrate ferric chloride performed better in COD reductions at low pH 5.0 and 5.5 (55% and 56%), while alum (9,000 mg/L) performed relatively better at pH 7.0 and 8.0, achieving 33% and 27% respectively.

Over 35% of turbidity was removed by adjusting the leachate pH from pH 7.0 to pH 10.0 before the coagulation process, as shown in Figure 4-23. A maximum turbidity reduction (54%) was observed at pH 10.0 at an alum dose of 7,000 mg/L. Aziz et al. (2007) also observed high turbidity removal results (82%) when treating a semi-aerobic landfill leachate at pH 12.0. An increase of over 200% in turbidity concentrations was observed at pH 7.0 and 8.0 with increasing alum doses. Generally, pH 9.0 and pH 10 did not show much change in turbidity reductions with increasing alum doses, as shown in Figure 4-23. Overall, hexahydrate ferric chloride performed better in turbidity reductions at low pH 5 and pH 5.5 (87% and 82%) than alum at high pH levels.

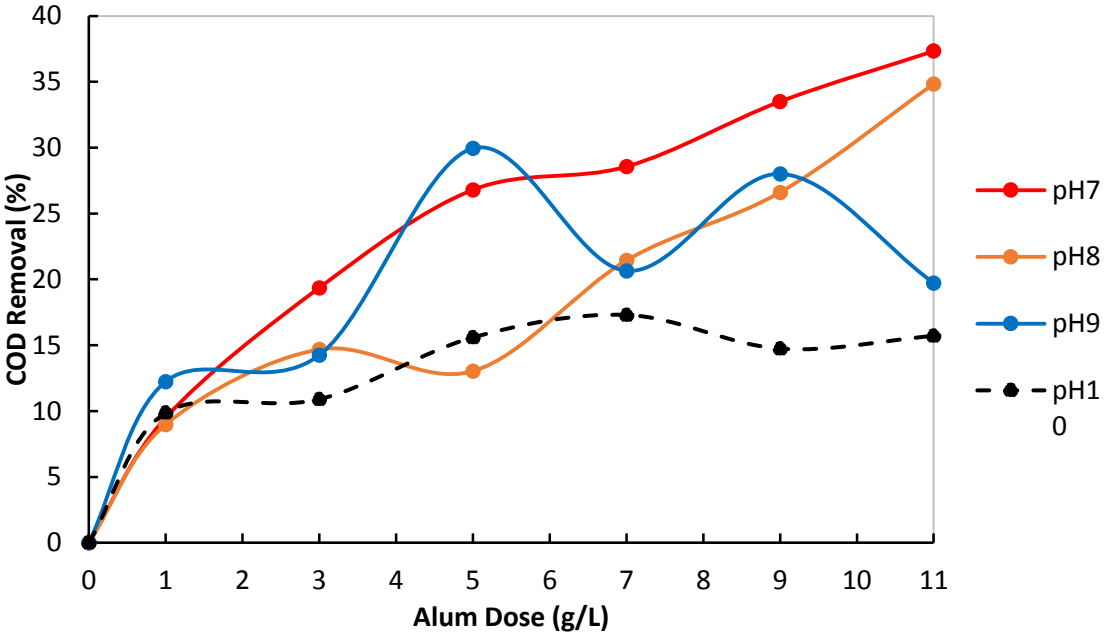


Figure 4-22: Effect of pH on COD removal at various alum dosages.

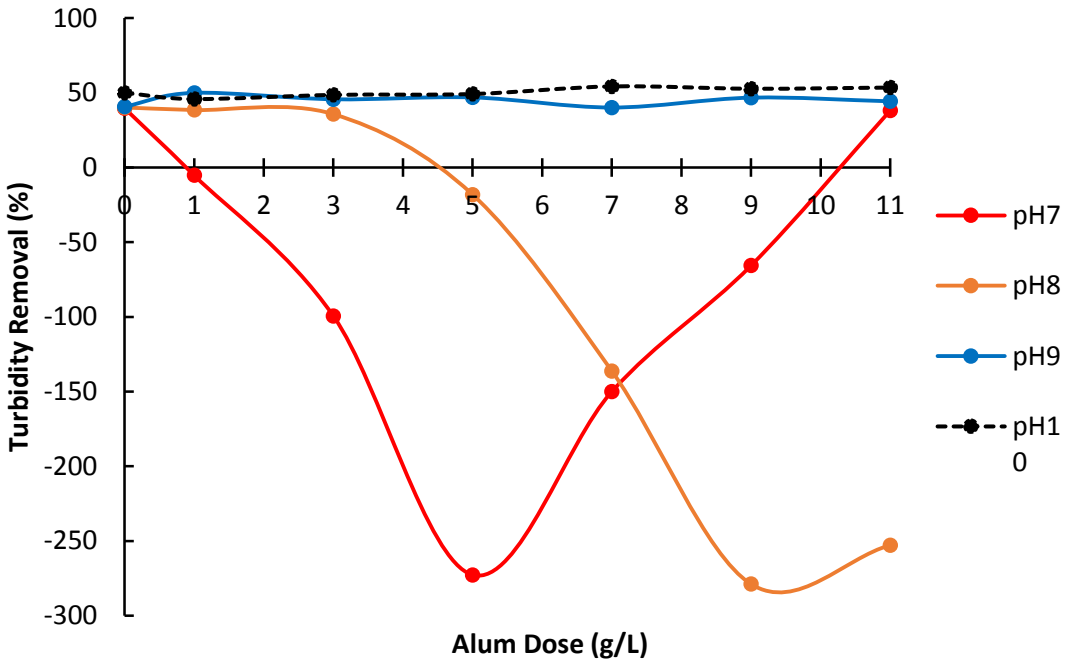


Figure 4-23: Effect of pH on turbidity removal at various alum dosages.

a) Initial pH and final pH with alum as a coagulant

In experiments where a biological process follows the coagulation–flocculation treatment, the final pH of the supernatant has to be considered and controlled. In biological experiments, the pH can limit the nitrification process by inhibiting the growth of nitrification (van Loosdrecht et al., 2016). According to van Loosdrecht et al. (2016) and Mihelcic and Zimmerman (2013) the nitrifiers (bacteria) thrive at pH between 7.5 and 8.5 but nitrification process can still take place at pH between 6.5 and 7.0. Therefore, this study also considered the final pH of the supernatant after coagulation–flocculation treatment. As shown in Figure 4-24, experiments at pH values between pH 9.0 and pH 10.0 yielded alkaline supernatants (> pH 8.5) which are likely to limit the nitrification process. Therefore, if such supernatants are to be used in a nitrification process, their pH levels will require adjustment to favourable conditions using hydrochloric acid. Experiments at pH 7.0 and pH 8.0 yield supernatants favourable for nitrification processes except experiments with alum dose values beyond 7,000 mg/L. These supernatants below pH 6.5 require adjustment with sodium hydroxide to raise the pH to conditions conducive to the growth of nitrification biomass (van Loosdrecht et al., 2016).

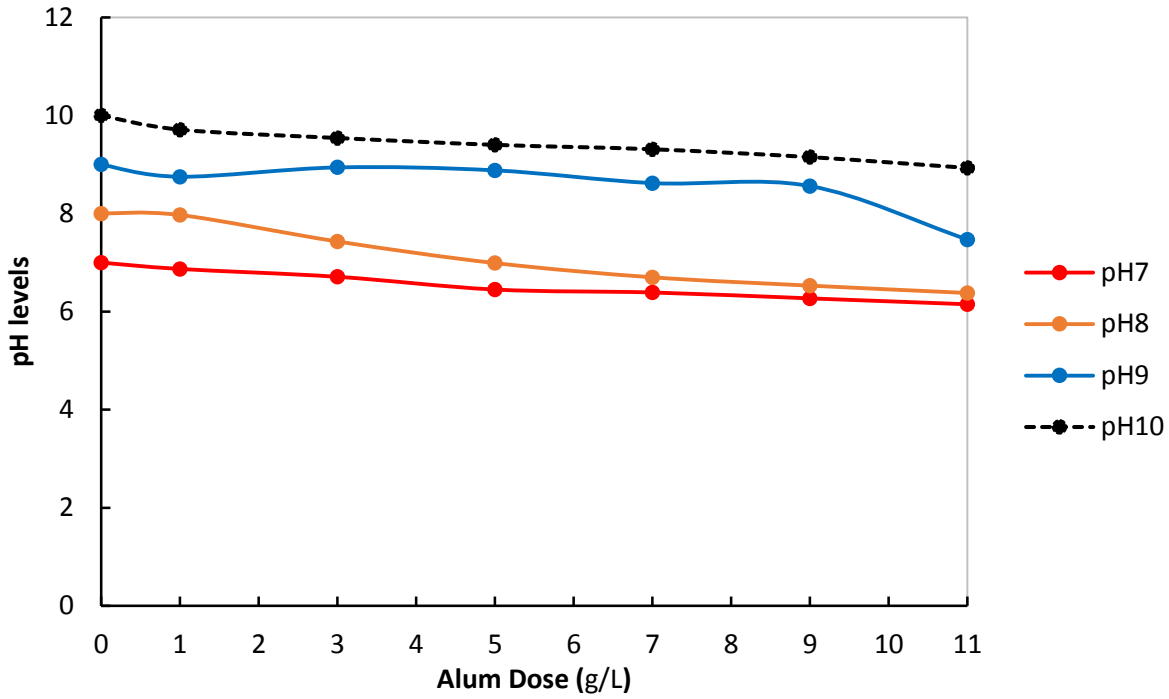


Figure 4-24: Supernatant final pH after coagulation–flocculation with various alum dosages.

4.3.5 Optimisation investigations

The coagulant doses were optimised for the effect of pH, mixing regimes and settling time. These investigations were conducted with hexahydrate ferric chloride only. The aim of the optimisation analyses was to establish the optimum conditions that yield the highest removal of ammonia nitrogen, COD and turbidity, with low sludge generation. Optimisation employed jar tests as batch analysis.

4.3.5.1 Effect of pH on coagulant dosage

Experiments were conducted without adjusting pH, at raw leachate pH (7.92) using different coagulant (hexahydrate ferric chloride) doses (0, 1.0, 1.5, 1.8, 2.0, 2.5, 3.0 and 3.5 g/L). This was to compare with the previous results after adjusting pH to pH 7.0. In these experiments, only NH_3-N was analysed from the supernatant. The results in Figure 4-25 shows that the reductions of NH_3-N with the raw leachate original pH (7.92) were very low (maximum of 7% at a coagulant dose of 5,000 mg/L) compared with those of pH 7.0 (9.5% at a coagulant dose of 3,000 mg/L). However, it was observed that the removal efficiency at pH 7.92 increased with increasing coagulant dose, achieving the highest value of 7.0% at a dose of 5, 000 mg/L. This results coincide with the report by Aguilar et al. (2002) indicating that the optimal pH for

iron salts ranges between 5.0 and 7.0. Moreover, NH_3-N analyses were carried out after adjusting the pH to pH 7.0 without any coagulant dose. An insignificant ammonia nitrogen removal of 4.0 % was observed, as shown Figure 4-25.

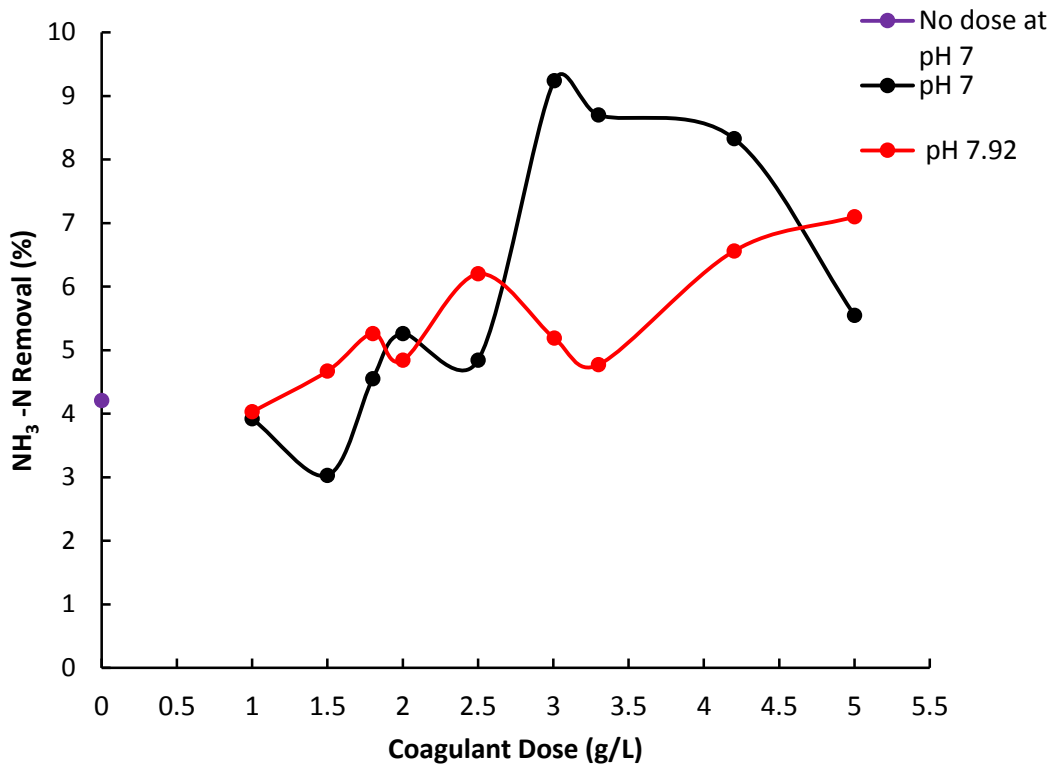


Figure 4-25: Effect of pH and hexahydrate ferric chloride ($FeCl_3.6H_2O$) dosages on ammonia nitrogen removal.

4.3.5.2 Effect of pH on optimal coagulant (hexahydrate ferric chloride) dose

In coagulation–flocculation, pH is a key variable. In acid conditions, metal coagulants dissociate in solution and release ions (Fe^{3+} or Al^{3+}) that are responsible for the coagulation process (Aziz et al., 2007; Tsatsi et al., 2003). These experiments were carried out by adding hydrochloric acid (1.0N) to adjust the raw leachate pH from 5.5 to 7.0, and 1.0N sodium hydroxide to adjust the leachate to pH 9.0. The coagulant (hexahydrate ferric chloride) doses were kept constant at 3,000 mg/L and the influence of pH was evaluated. The supernatant was analysed for NH_3-N, COD and turbidity. Also, the wet sludge volume generation was observed to monitor the influence of pH on its production. As shown in Figure 4-26, high NH_3-N removal of 16% and 16.1% were observed at low pH 5.0 and high pH 9.0 respectively. In addition, high NH_3-N removals of 16% and 10.2% were still observed without the addition of a coagulant (0 mg/L) at low pH 5.0 and high pH 9.0 respectively. These NH_3-N removals (16% and 10.2% at

0 mg/L) happened in the absence of sludge formation. A likely possible cause of these results could be the analytical problems by the machinery or any other possible reason not investigated by this study. According to Terry et al. (1978), at pH 9.0 there is an increase of OH^- concentration in the solution that causes the shift of the NH_4^+ and NH_3 dynamic equilibrium, hence favouring the loss of NH_4^+ by volatilisation (as gaseous NH_3). However, at pH 5.0, the dynamic equilibrium shifts in favour of NH_4^+, hence volatilisation will not take place (Terry et al., 1978). Therefore, this study could not attribute the loss of ammonium at pH 5.0 (0 mg/L) to any factor. As the pH levels were varied from 5.0 to 6.5, a decrease in NH_3-N removal was observed both with and without coagulant dose.

A similar removal pattern was noticed with COD in Figure 4-27. About 55% and 56% COD removals were observed at the lower pH value of pH 5.0 and pH 5.5 respectively. Thereafter, a decrease in COD removal was observed from pH 6.0 (27%) to pH 9.0 (9.5%). Turbidity results also agrees with NH_3-N removal, however turbidity analyses were conducted only on supernatants after coagulation–flocculation. Highest turbidity removals were observed at pH 5.0 (87%) and pH 5.5 (82%), as shown in Figure 4-27. Similar high turbidity results were achieved in different studies: both Aziz et al. (2007) and Marañón et al. (2010) observed turbidity removal of 94% each with ferric chloride at pH 4.0 and pH 5.0 to 5.5 respectively.

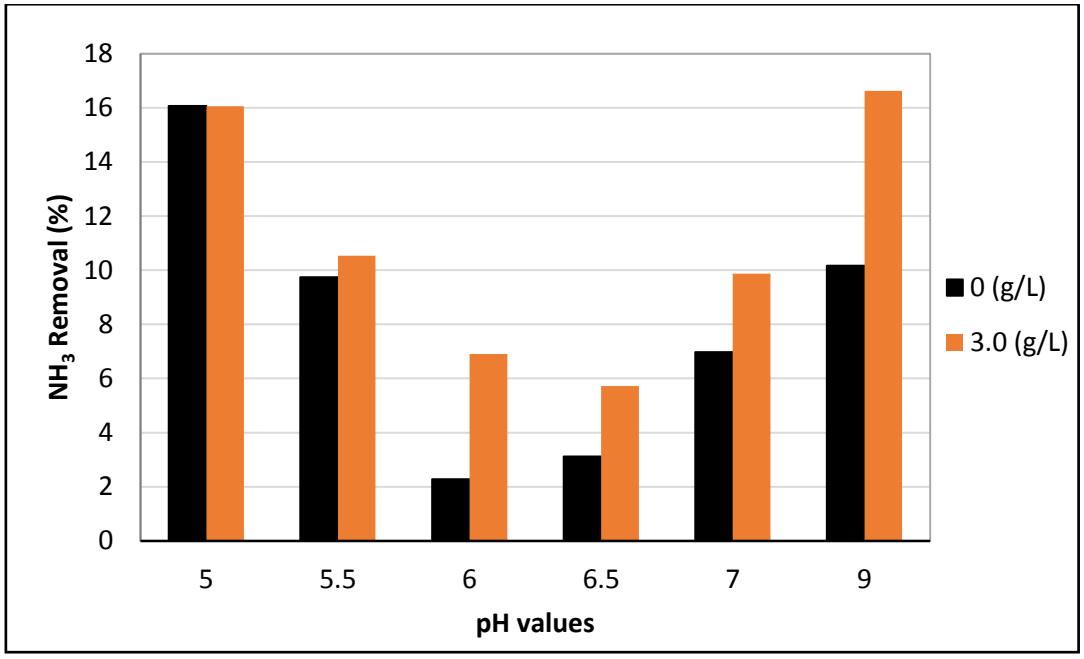


Figure 4-26: Effect of pH on ammonia nitrogen removal with and without $FeCl_3.6H_2O$.

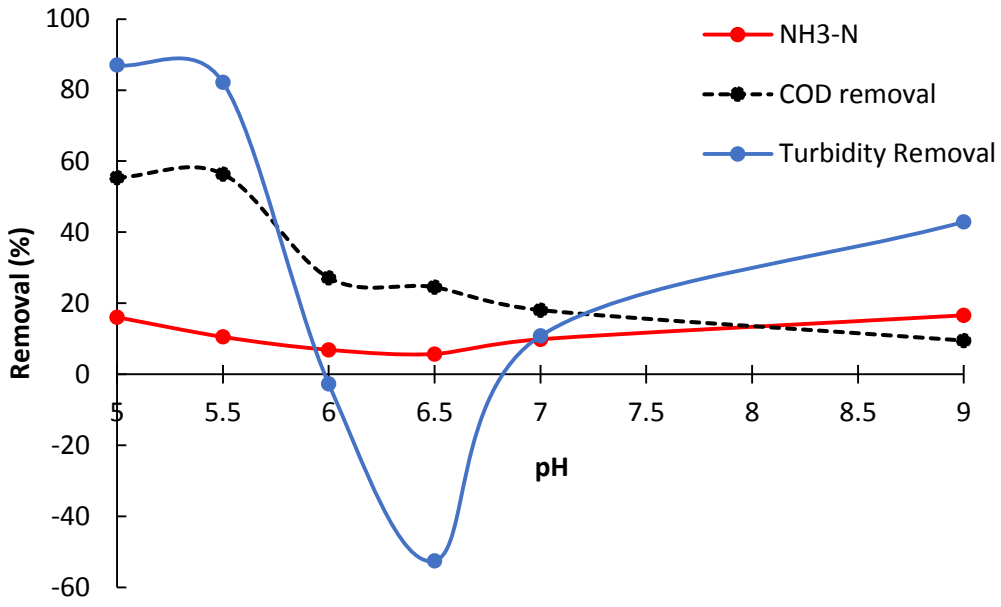


Figure 4-27: Effect of pH on NH_3-N, COD and turbidity removal at 3.0 g/L of $FeCl_3.6H_2O$.

4.3.5.3 Wet sludge volume

No sludge was produced by adjusting leachate pH without a coagulant addition. However, NH_3-N removals of 16% and 10.2% were still observed without the addition of a coagulant at low pH 5.0 and high pH 9.0 respectively (Figure 4-26). As mentioned earlier the likely possible cause of these results could have been analytical problems by the machinery or any other possible reason not investigated by this study. The wet sludge volume produced by these experiments was estimated to be between 16% and 40% of the total treated leachate volume across the coagulant dose. High sludge generation (40%) was observed after coagulation process at pH 5.5 and the lowest (16%) was observed at pH 6.5. More information on these experiments is captured on Table 4-4 and Figure 4-28.

Table 4-4: Effect of pH on Sludge Production with and without $FeCl_3.6H_2O$.

Coagulant	**Coagulant dose** (mg/L)	**Sample pH**	**Wet sludge volume** (%)	**Comment/Observations**
Hexahydrate ferric chloride	0	5.0	None	Foams during pH adjustment, no colour changed, no flocs formed.
	3,000	5.0	23	Foams during pH adjustment and coagulation, colour reduced, 23% flocs, grey flocs formed.
	0	5.5	None	Foams during pH adjustment, no colour changed, no flocs formed.
	3,000	5.5	40	Foams during coagulation, colour reduced, 40% flocs, grey flocs formed.
	0	6.0	None	Foams during pH adjustment, no colour changed, no flocs formed.
	3,000	6.0	23	Foams during coagulation, no colour changed, 23% flocs, grey flocs formed.
	0	6.5	None	Foams during pH adjustment, no colour changed, no flocs formed.
	3,000	6.5	16	Foams coagulation, co colour change, 16 % flocs, grey flocs formed.
	0	7.0	None	No foaming, no colour changed, no flocs formed.
	3,000	7.0	30	No foaming during coagulation, slight colour reduced, 30% flocs, and grey flocs formed.
	0	9.0	None	Foaming, no colour changed, no flocs formed.
	3,000	9.0	20	No foaming during coagulation, colour reduced, 20% flocs, brown flocs.

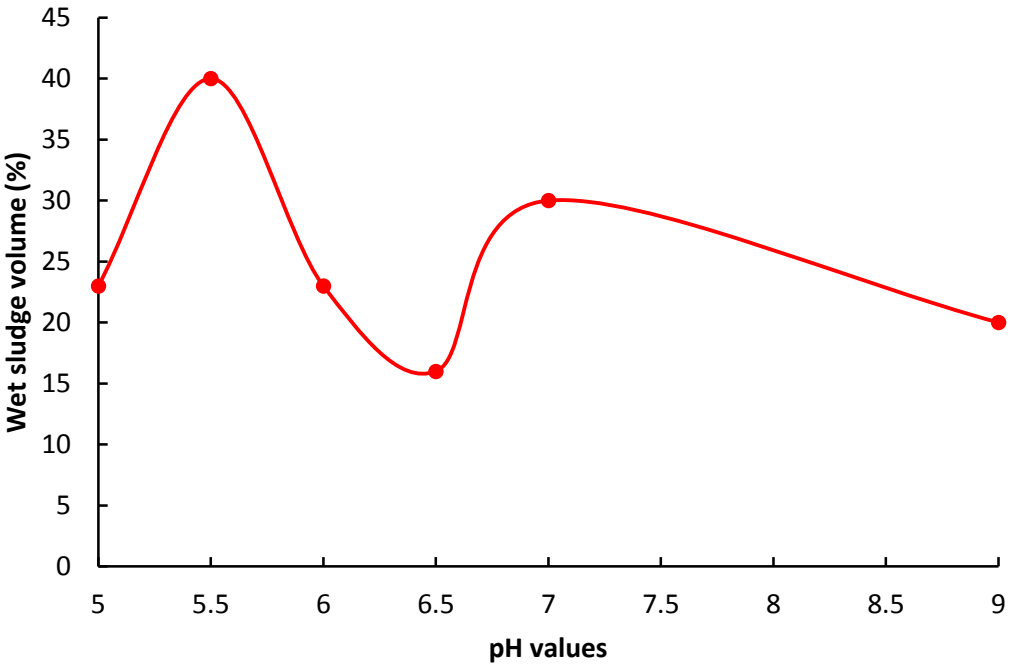


Figure 4-28: Effect of pH on sludge production at 3.0 g/L of $FeCl_3.6H_2O$.

4.3.5.4 Effect of varying mixing regimes

Optimisation of the coagulation–flocculation process depends on the mixing regime. The objective of coagulation is to destabilise the colloids using a coagulant. Particle destabilisation involves particles transported to the contact site and particle destabilisation (Kang, 1994). Destabilisation is based on rapid speed and long mixing time used to achieve a complete mixing of leachate/wastewater with coagulants. In these experiments the mixing speed and mixing time varied from 70 to 600 rpm and 1 to 15 minutes, respectively. Rapid mix was followed by flocculation, where slow mixing was used to enhance the contact between destabilised particles. The flocculation stage is used to promote the growth of the destabilised floc by promoting particle to particle contact (Kang, 1994). The slow mixing speeds and slow mixing time varied from 10 to 60 rpm and 5 to 30 minutes respectively. Thereafter the particles were allowed to settle by gravity for 10 to 300 minutes. The mixing base conditions are presented in Table 4-5.

Table 4-5: Base Conditions for The Mixing Regimes with $FeCl_3.6H_2O$ at pH 7.0.

Mixing regime effects	**Conditions**	**Dose** (mg/L)	**Rapid mixing time** (minutes)	**Rapid mixing speed** (rpm)	**Slow mixing time** (minutes)	**Slow mixing speed** (rpm)	**Settling time** (minutes)
Effects of rapid mixing speed and mixing time on treatment	Varying rapid mixing speed	3,000	4	70–600	20	30	30
	Varying rapid mixing time	3,000	1–15	100	20	30	30
Effects of slow mixing speed and slow mixing time on treatment	Varying slow mixing speed	3,000	4	100	20	10–60	30
	Varying slow mixing time	3,000	4	100	5–30	30	30
Effects of settling time on treatment	Varying settling time	3,000	4	100	20	30	10–300

a) Effects of rapid mixing speed and rapid mixing period

Figure 4-29 shows the effect of various mixing speeds on NH_3-N, COD and turbidity removal with optimal dose of $FeCl_3.6H_2O$. It was observed that varying the mixing speeds did not improve the NH_3-N removal as <9.0% was achieved. The mixing speeds between 70 and 200 rpm produced very similar NH_3-N reduction results, while beyond 200 rpm less than 7.0% of NH_3-N removal was achieved. Complete mixing occurs at rapid mixing speeds; however, very

high mixing > 200 rpm disturb the process of complete mixing of particles, hence affecting the treatment efficiency (Kang, 1994). A similar pattern was observed with COD reductions. Low (13.7%) COD reductions were achieved at 70 rpm, while at 100 rpm and beyond, very similar reductions of less than 17% were observed. High turbidity reductions (23.6%) were obtained at 70 rpm, and thereafter lower reductions were observed with increasingly rapid mixing speeds.

A similar removal pattern was also noticed with rapid mixing time in Figure 4-30. Maximum reductions of 8.9% of NH_3-N, 16.9% of COD and 11.5% of turbidity were achieved at an optimum rapid mixing time of four minutes. All the rapid mixing times investigated (1, 4, 10 and 15 minutes) exhibited similar NH_3-N and COD removal patterns. However, turbidity reductions decreased with increasing rapid mixing times, showing a 62.8% increase in turbidity of the solution at 15 minutes. For these experiments, the rapid mixing regime did not improve NH_3-N, COD and turbidity removals.

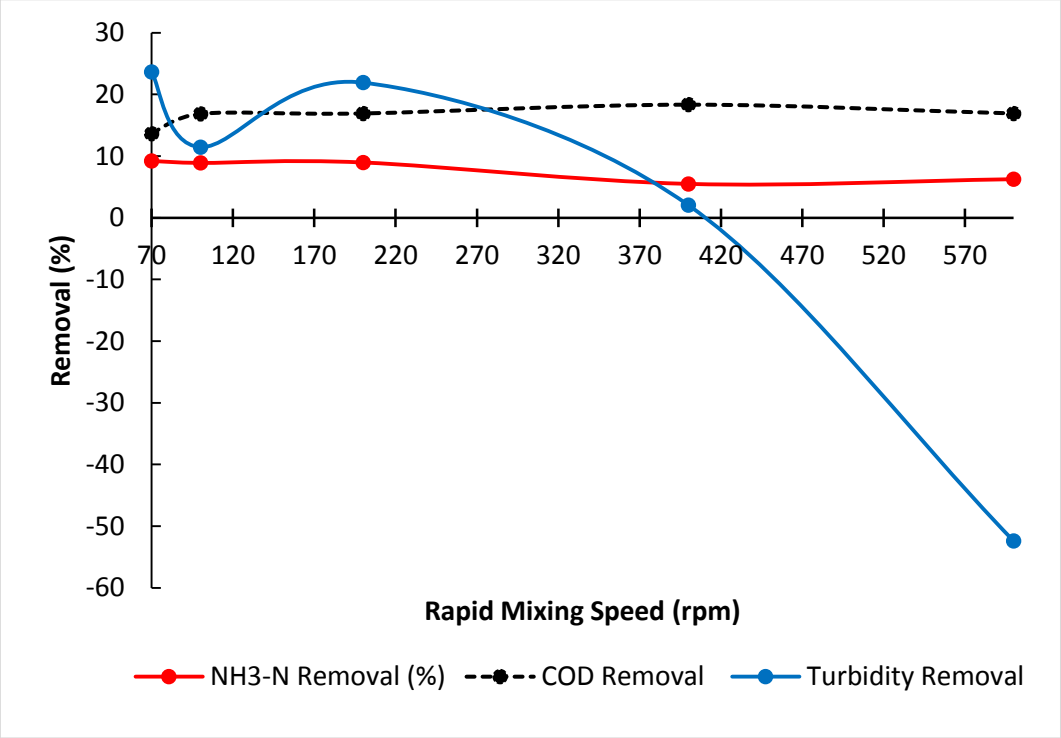


Figure 4-29: Effect of rapid mixing speed on NH_3-N, COD and turbidity removal, at 3.0 g/L of $FeCl_3.6H_2O$. Rapid mixing time, slow mixing regime and settling time were fixed (*Table 4-5*).

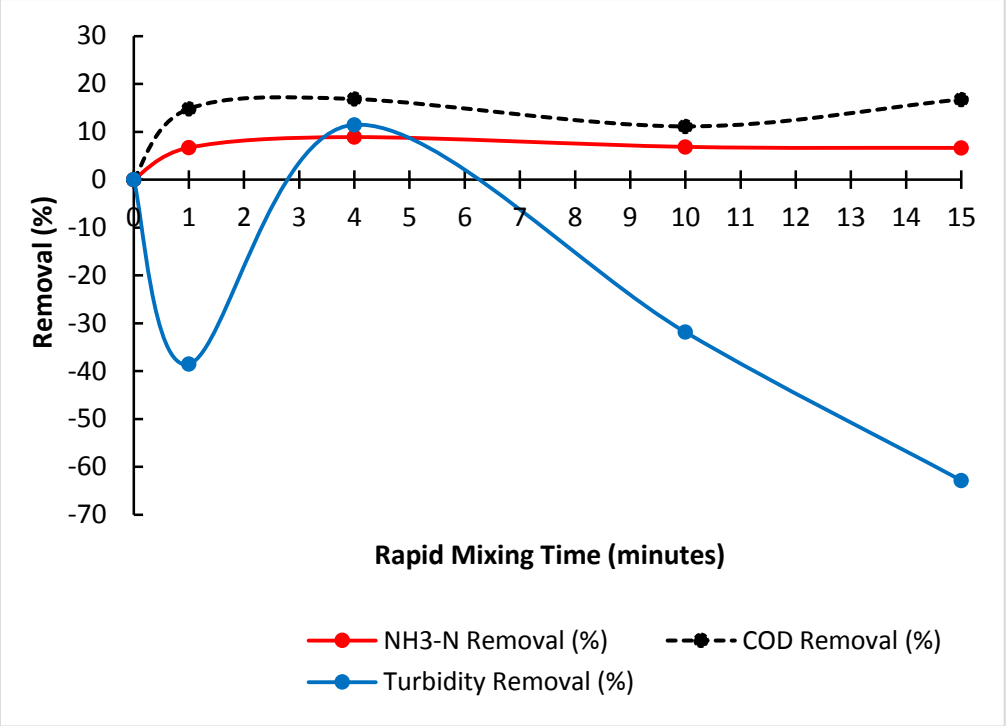


Figure 4-30: Effect of rapid mixing time on NH_3-N, COD and turbidity removal, at 3.0 g/L of $FeCl_3.6H_2O$. Rapid mixing speed, slow mixing regime and settling time were fixed (*Table 4-5*).

b) Effects of slow mixing velocity and slow mixing time

A similar removal pattern was also noticed with slow mixing speed as shown in Figure 4-31. A maximum of 9.0% NH_3-N, 17% COD and 18.0% turbidity reductions were achieved at an optimum slow mixing speed of 30 rpm. All the slow mixing times investigated (10, 20, 30 and 60 minutes) exhibited similar NH_3-N and COD removal patterns. However, turbidity reductions decreased with increasing slow mixing speed showing an increase of 11.0% of turbidity in the solution at highest speed.

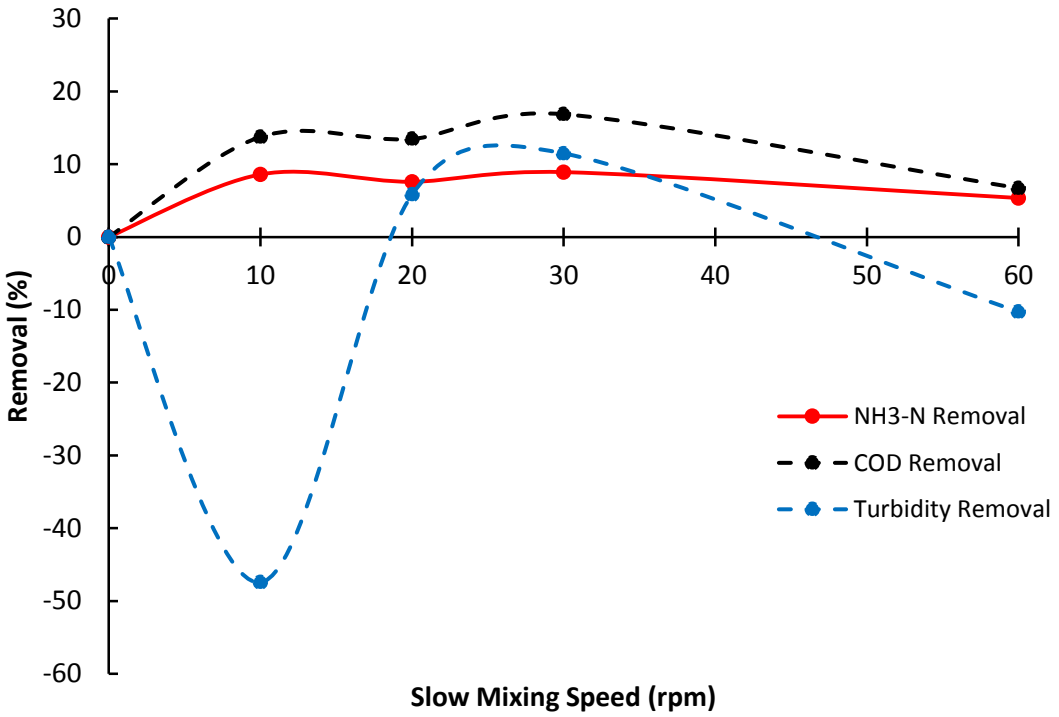


Figure 4-31: Effect of slow mixing speed on NH_3-N, COD and turbidity removal, at 3.0 g/L of $FeCl_3.6H_2O$. Slow mixing time, rapid mixing regime and settling time were fixed (*Table 4-5*).

The results of changing the slow mixing time are presented in Figure 4-32. The pollutant reductions increased with longer slow mixing times, obtaining maximum reductions of 9.0% NH_3-N, 17.0% COD and 12.0% turbidity at slow mixing time of 20 minutes. The removal efficiency was then reduced after 20 minutes of slow mixing, showing a low of 8.0% for NH_3-N and 15.0% for COD. A similar removal pattern was also noticed with turbidity, eventually producing an increased turbidity at 30 minutes. In short, these experiments with a slow mixing regime did not improve NH_3-N, COD and turbidity removals.

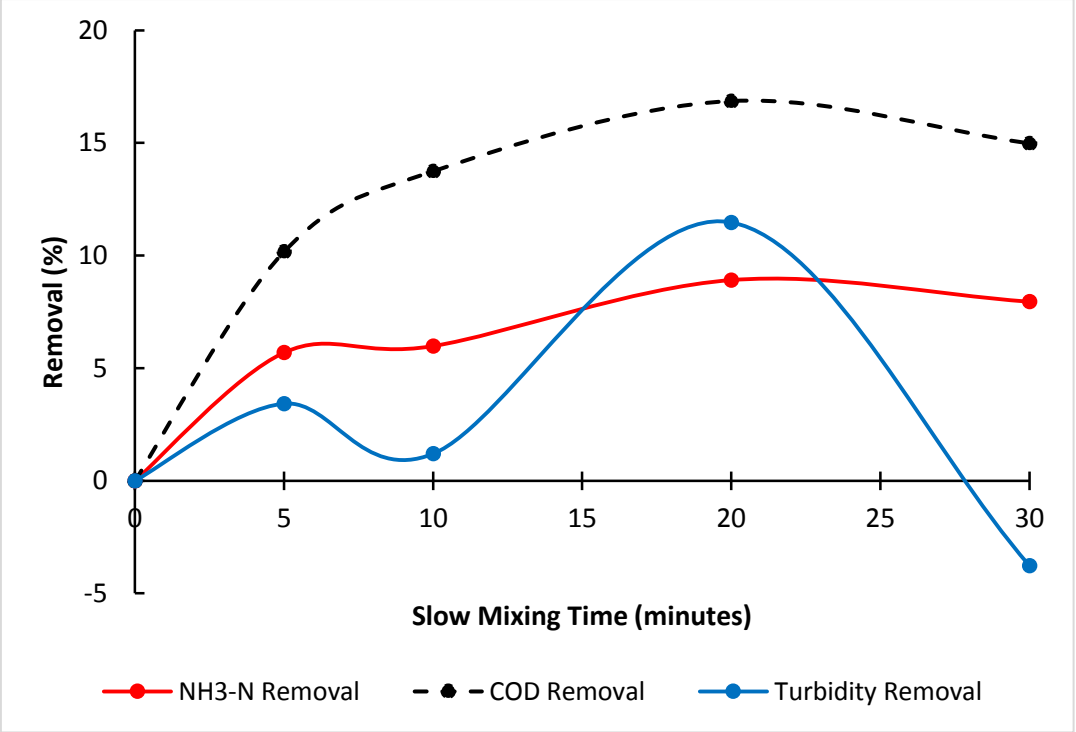


Figure 4-32: Effect of slow mixing time on NH_3-N, COD and turbidity removal, at 3.0 g/L of $FeCl_3.6H_2O$. Slow mixing speed, rapid mixing regime and settling time were fixed (*Table 4-5*).

c) Effects of settling period

As shown in Figure 4-33 a maximum of 10.0% NH_3-N, 17.0% COD and 12.0% turbidity reductions were achieved at an optimum settling period of 30 minutes. These experiments exhibited similar NH_3-N, COD and turbidity removal patterns. However, increase in turbidity concentrations were observed at settling times between 50 to 290 minutes. Thereafter, only 3.4% turbidity removal was observed. In summary, long settling periods also did not improve NH_3-N, COD and turbidity removals.

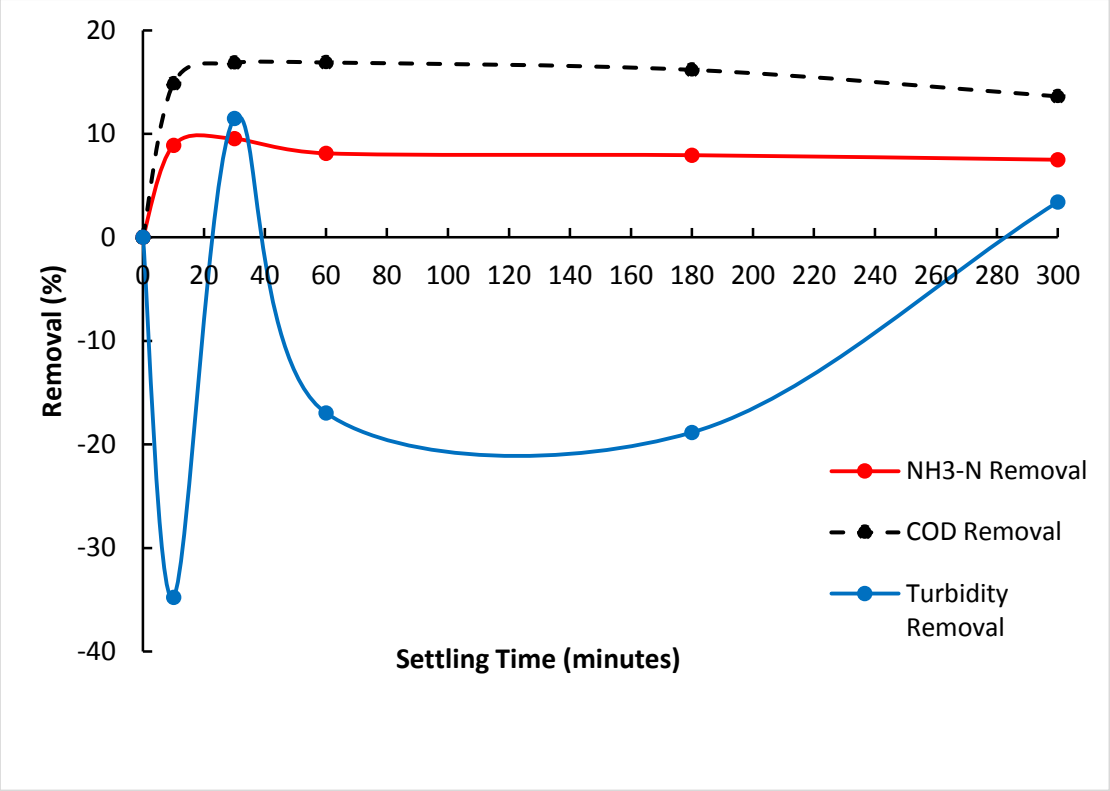


Figure 4-33: Effect of settling time on NH_3-N, COD and turbidity removal, at 3.0 g/L of $FeCl_3.6H_2O$. Rapid mixing speed regime and slow mixing regime were fixed (*Table 4-5*).

Optimisation of the coagulation–flocculation process is known to depend on the mixing regime. However, in these experiments varying mixing regimes did not have much effect on NH_3-N removal. This is likely because of the non-colloidal matter nitrogen exhibit in the solution.

4.4. Conclusion

Coagulation–flocculation results from the first and second batch experiments at pH 7.0 showed that anhydrous ferric chloride was a better coagulant than alum in treatment of landfill leachate. The first batch experiment results showed 36.5% and 14.5% NH_3-N reductions with anhydrous ferric chloride and alum respectively. Moreover, 50.7% COD and 76.7% colour reductions were achieved with anhydrous ferric chloride at low dose (2,000 mg/L and 3,500 mg/L respectively), while alum achieved 36% COD and 88.1% colour reductions only at high doses (14,000 mg/L each). Furthermore, anhydrous ferric chloride showed a 47.0% reduction in turbidity, while alum caused an increase in turbidity concentrations with increasing alum doses from 1,000 to 14,000 mg/L. The second batch experiments were conducted at a later stage with only anhydrous ferric chloride to confirm the first batch results. These experiments observed a

maximum of 20.4% and 28.5% of NH_3-N and COD removal respectively at a dose of 2,000 mg/L. In summary, these experiments obtained low results as compared to the second batch results with anhydrous ferric chloride. However, these experiments still exhibit anhydrous ferric chloride as a more effective coagulant than alum in treatment of landfill leachate.

However, a change in the percentage removal of pollutants (NH_3-N, COD and turbidity) was observed with hexahydrate ferric chloride at similar doses and pH (7.0). The highest reductions in NH_3-N, COD and turbidity achieved by hexahydrate ferric chloride ($FeCl_3.6H_2O$) were 9.0%, 26% and 38.7% respectively. The interaction of cationic polyelectrolytes (Magnesol 598, Crystalfloc and Magnafloc LT7991) and $FeCl_3.6H_2O$ was also investigated. A decline in NH_3-N removal was observed with the addition of cationic polyelectrolytes. A similar pattern was observed with COD reductions. However, a combination of 3,000 mg/L of $FeCl_3.6H_2O$ and 5 ml/L of Magnesol 598 obtained a maximum COD reduction of 45.0%. Moreover, the interaction between FeCl3.6H2O and Magnesol 598 showed a good performance in turbidity removal compared with other combinations: a maximum of 93.7% turbidity removal was achieved at 3,000 mg/L of $FeCl_3.6H_2O$ and 30 ml/L of Magnesol 598.

Experiments with the optimisation of pH achieved 17.0%, 16.0%, 11.0% and 10.0% reductions of NH_3-N with pH values of pH 9.0, pH 5.0, pH 5.5 and pH 7.0 respectively. However, experiments at pH 5.0 and 5.5 were not ideal for this study due to their impracticability, while pH 9.0 caused volatilisation of free ammonia, therefore this pH was not also ideal for this study. Experiments with varying pH (from pH 7.0 to pH 10.0) and varying coagulant doses were also conducted with alum. However, experiments at pH 9.0 to 10.0 were suspected of volatilisation of free ammonia and were considered not ideal for this study. Experiments at pH 7.0 and 8.0 showed high NH_3-N removals of 10.7% and 11.9% respectively, at a high dose of 11,000 mg/L with alum. These pH values (7.0 and 8.0) also achieved maximum COD reduction of 37.3% and 34.8% respectively at a dose of 11,000 mg/L of alum.

Therefore, based on optimisation, the ideal coagulant found by this study was hexahydrate ferric chloride, achieving 10.0% reduction of NH_3-N at the optimal pH value of pH 7.0 and at an optimal dose of 3,000 mg/L. However, generally, anhydrous ferric chloride exhibited higher NH_3-N removal of over 20% optimal pH value of pH 7.0 and at a dose of 2,000 mg/L. Therefore, based on these results, this study consider anhydrous ferric chloride an ideal coagulant for treating NH_3-N from landfill leachate through coagulation–flocculation method.

The use of anhydrous ferric chloride for treating NH_3-N from landfill leachate through coagulation–flocculation method will only reduce NH_3-N from leachate by ≈20.0% (from 2,260 mg/L to 1,808 mg/L). This leachate still contains very high NH_3-N concentrations, not friendly to the environment and therefore very toxic to aquatic life in receiving water bodies. This leachate would still potentially deplete dissolved oxygen and contribute to eutrophication and in the surrounding water bodies. Most importantly, this leachate would still impact negatively on the wastewater treatment processes hence the landfill owners would still be charged for treating their leachate at wastewater treatment plants. Overall, NH_3-N treatment through coagulation–flocculation alone would still retain all the initial leachate concerns in the environment, therefore not ideal. Therefore, the possibility of treating ammonia nitrogen through an integrated system of coagulation–flocculation with another option could be ideal.

CHAPTER 5. Adsorption method: Option 2

For this study, the aim is to investigate the adsorption potential of local soils mainly found within the landfill site and their suitability for ammonia nitrogen removal from landfill leachate. Zeolite soil was also investigated. However, the use of zeolite allows a check to see the best likely adsorption performance. It might not be cost effective to use zeolite, but gives an idea of what might be achieved, and allows comparison of the site-specific soils to a reference material that we know has been used to remove ammonia.

5.1 Materials and methods

5.1.1 Local soils (sorbents)

Four different disturbed soil samples were obtained from a local landfill site using a shovel or soil auger and immediately sealed in one-litre plastic containers as shown in Figure 5-1. These soils were type A, type B, type C (sediment from a water storage pond), and type D (sediment from a stormwater sedimentation pond). The soils were immediately transported to the University of Canterbury environmental laboratory and refrigerated to 4ºC. This was to prevent the organic matter component of the soils from decomposing, which could be important in ammonia nitrogen removal. Most of these soils are associated with having high organic matter, which has the potential to assist in the removal of ammonia nitrogen. Virtually, type C soil is very dark in colour with approximated organic content of 5% while type D has a dark colour with an approximate organic content of 3.5%, as shown in Table 5-1. These colours were identified virtually and then matched with their organic contents as shown in Table 5-1. Soils with higher clay content are expected to assist with ammonia nitrogen sorption. Types A and B were sampled near calcium carbonate rocks. Calcium carbonate is also very important in the removal of ammonia nitrogen. High calcium carbonate in the soil could raise the leachate pH, and hence facilitate ammonia nitrogen removal.

Figure 5-1: Well sealed soils from a local landfill site.

Table 5-1: Soils Characteristics. Adapted from USDA web.

Soil type	Colour	Organic matter (%)
A	light	2.0
B	Light	2.0
C	Dark	3.5
D	Very dark	5.0

5.1.1.1.Preparation of local Soils

The four soil samples were kept and dried in a temperature controlled room (about 25 ºC and 20 % humidity) for about seven days as shown in Figure 5-2. Following drying, the samples were then milled into very fine small particle sizes using IKA A11 basic hand mill as shown in Figure 5-3. Before grinding, stones, twigs, big particles and other organic content were removed as oversize to prevent malfunctioning of the mill. Coarse particles of about 10 mm and above in size usually lock the mill motor hence destroying the efficiency of the mill. Thereafter, the ground samples were put back into the controlled temperature room for another seven days complete drying before adsorption analysis. Finally, the samples were sealed into respective 1 L containers ready for analysis. Grinding/milling the soil samples increases the particles surface area relative to their volume.

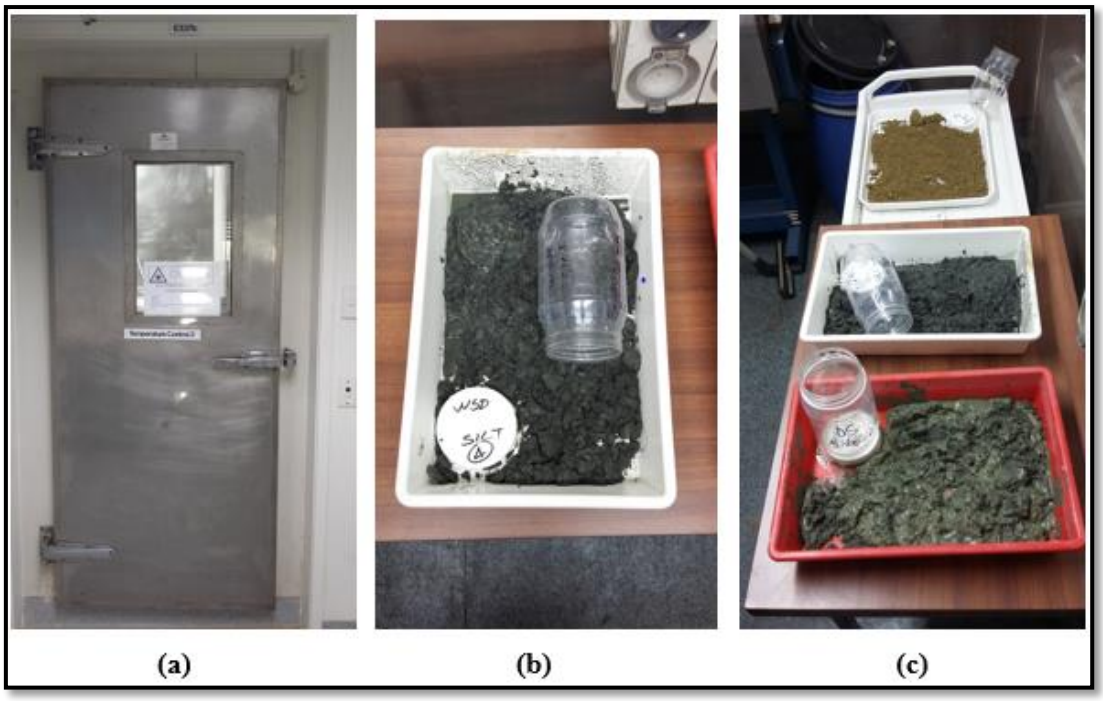


Figure 5-2: Soils sample drying up in a temperature controlled room: (a) temperature control room, (b) Type C spread in a tray for drying and (c) local soils drying in temperature control room.

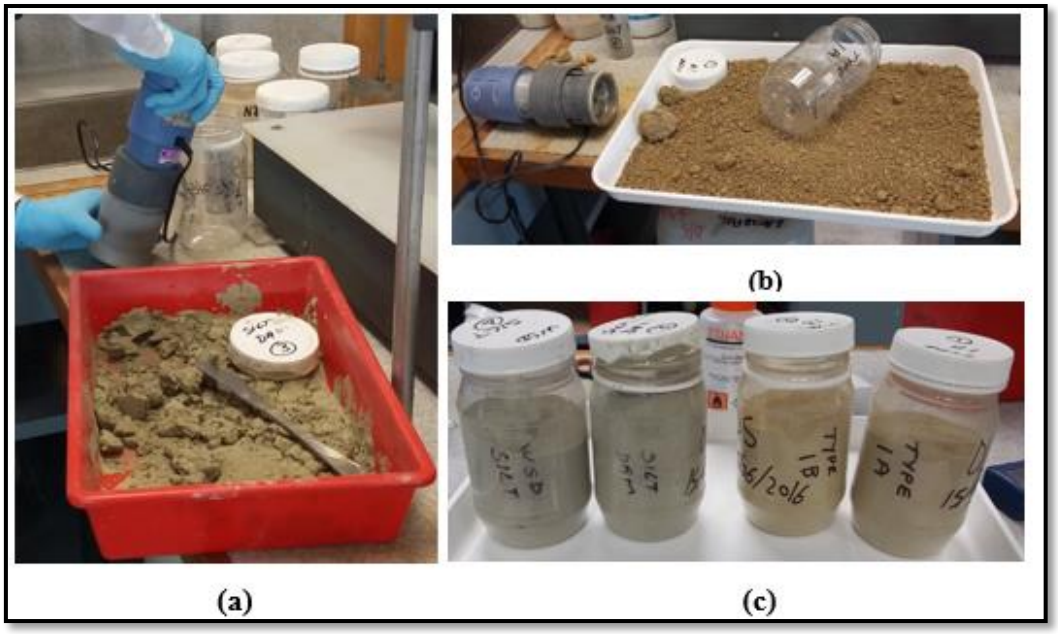


Figure 5-3: (a) & (b) Sample ready for milling. (c) Four soil sampled milled and ready for second drying.

5.1.1.2.Local Soils chemical and physical analyses

The mineralogical parameters of the four soil samples were extracted from a confidential hydrological investigation report conducted by the same local landfill from which they were sourced. The characteristics are presented in Table 5-2. Moreover, particle size distribution of the soil samples was determined using a sedimentation process with 151H and 152H hydrometers at the University of Canterbury geomechanics laboratory. The particle size distribution analyses were conducted according to the standard test method for particle size analysis of soils: ASTM standards D422-63 (2007). Seven glass cylinders of 1000 mL volume and 63.5 mm diameter were employed in the sedimentation process based on E100 specifications of the ASTM hydrometers (Figure 5-4). A sodium hexametaphosphate solution was used to disperse the soil samples for 24 hours (Figure 5-4a). Thereafter, the settling of each soil sample was determined at various time intervals for 24 hours. The very fine particles were then removed by washing with water and oven dried at 105˚C for 24 hours. Following the sedimentation process the soil samples were sieved (Figure 5-6) using a set of sieves as follows:

- No. 8 (2.36mm)
- No. 16 (1.18 mm)
- No. 30 (600 µm)
- No. 40 (425 µm)
- No. 50 (300 µm)
- No. 100 (150 µm)
- No. 200 (75 µm)

A summary of sieve analysis results is presented in Table 5-3. The AASHTO soil classification system (clay: <0.002 mm, silt: 0.002–0.06 mm and sand: 0.06–2 mm) was used to classify the soil samples used in this study. From the table, soil type A is composed of 15% clay, 51% silt and 34% sand therefore, classified as sandy SILT. Soil type B is similarly classified as silt SAND (13% clay, 39% silt and 48 % sand). Type C soil consist of 6% clay, 71% of sand and 22% of silt hence classified as SAND with some silt whereas, type D is silt SAND (17% clay, 36% silt and 47% sand). Finally, zeolite used had 39% clay, 51% silt and 9% sand. The higher the clay and silt components in a soil sample the more affinitive the particles are to ammonia nitrogen ions. The particle size distribution curve of each soil sample from sieve analysis and the hydrometer data sheets are presented in Appendix J.

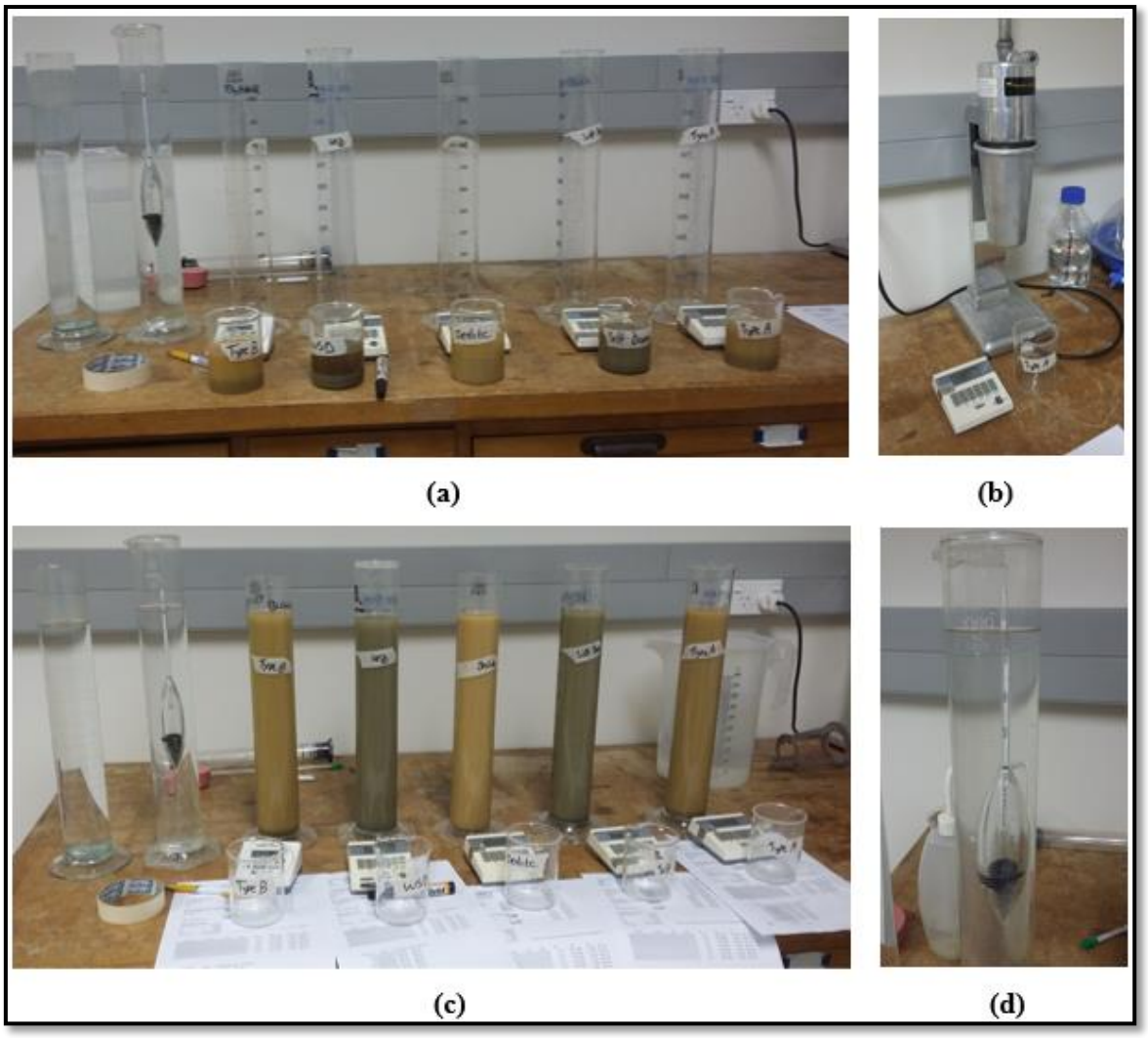


Figure 5-4: (a) Soils sample particles being dispersed with sodium hexametaphosphate solution. (b) Sample being agitated before sedimentation process. (c) Soil samples in glass cylinders and with timers ready for sedimentation process. (d) Hydrometer reading blank– distilled water for quality control.

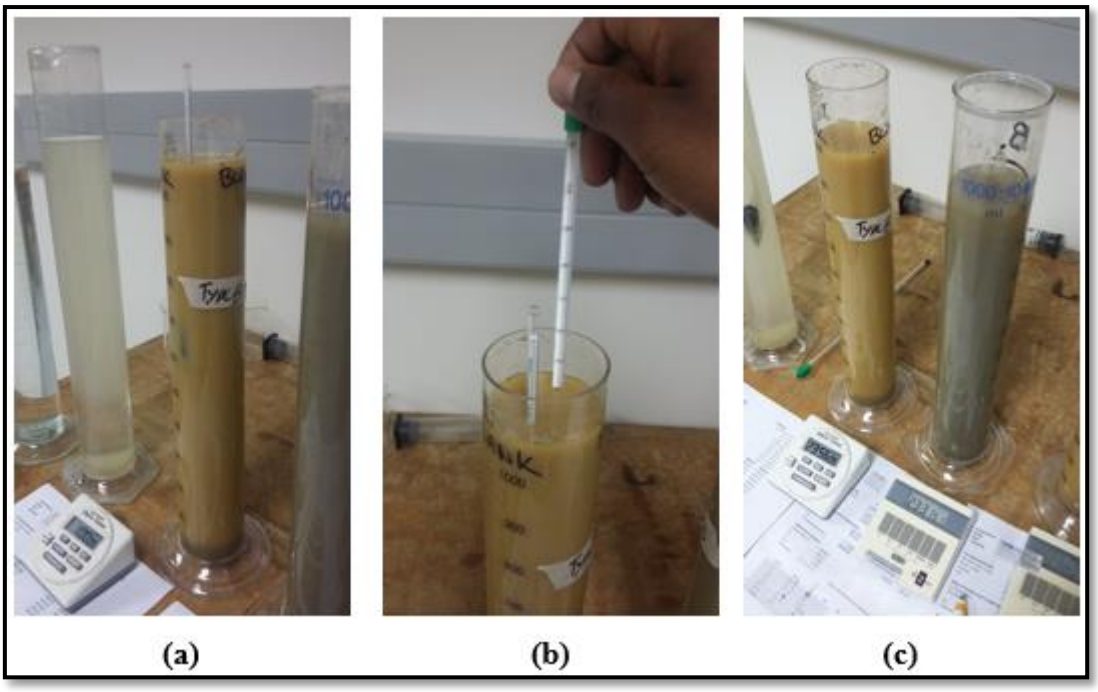


Figure 5-5: (a) Taking settling reading on soil type A at two minutes (b) Taking settling and temperature readings on soil type A at two minutes (c) Type B and type C soil samples awaiting settling and temperature readings at 24 hours' time.

Figure 5-6: All the soil samples undergoing sieve analysis.

Table 5-2: Local Soils Characteristics. (Adapted from local landfill hydrological investigation report).

	Description/Value			
Soil type	Type A	Type B	Type C	Type D
Characteristic				
Odour	No odour	No odour	No odour	No odour
pH	8.5	8.55	8.65	8.60
Cationic Exchange Capacity (CEC), meq/100 g	6.0	6.0	1.2–5.6	1.2–5.6
Total porosity, %	28 – 36	28 – 36	28–36	28–36
Total nitrogen, %	< 0.03	< 0.03	< 0.52	< 0.52
Bulk density, t/m^3	1.73 - 1.90 t/m^3	1.73 - 1.90 t/m^3	1.78–1.90	1.78–1.90
Quartz (SiO_2), (%)	<10	<10	10 – 52	10 – 52

Table 5-3: Summary of Soils Classification Results From Sieve Analysis.

Soil type	**Clay %**	**Silt %**	**Sand %**	**Classification**
Type A	15	51	34	Sandy SILT
Type B	13	39	48	Silty SAND
Type C	7	22	71	Silty SAND
Type D	17	36	48	Silty SAND
Zeolite	40	51	9	Clay SILT

5.1.2 Zeolite (sorbent)

Zeolite was used as a guide and to check for the effectiveness of adsorption on ammonia removal from the leachate. The zeolite used in this study was supplied by Blue Pacific Minerals Company in the Central North Island of New Zealand. The very zeolite was milled and prepared by the supplier (Blue Pacific minerals) with most of particle size ranging from silt to clay (see results on Table 5-3 and Appendix J. The most important property is its ammonia exchange capacity (AEC) and CEC with values range of 88–118 meq/100 g and 70–97 meq/100 g respectively. Its surface area ranges from 25–58 m2/g. More details are shown in Table 5-4 and the data sheet in Appendix K.

Table 5-4: New Zealand Zeolite Characteristics. (Adapted from Safety data sheet and Blue Pacific Minerals web page – www.bpmnz.co.nz).

Characteristic	**Description/Value**
Appearance	Fine dust, of white/tan colour
Odour	No odour
pH	8.65
Cationic Exchange Capacity (CEC), meq/100 g	70-97
Ammonia Exchange Capacity (AEC), meq/100 g	88–118
Internal surface area, m^2/g	25–58
Specific gravity/density, g/cm^3	0.65
Silicon dioxide, w/w %	< 10.0
Aluminium oxide, mg/m^3	10.0
Iron (II) oxide, mg/m^3	5.0
Magnesium oxide, mg/m^3	10.0
Calcium oxide, mg/m^3	2.0
Titanium dioxide, mg/m^3	10.0
Quartz (SiO_2), mg/m^3 • Quartz, respirable dust • Cristobalite, respirable dust	 0.2 0.2

5.2 Experimental method

For each soil sample, batch adsorption of ammonia nitrogen removal was investigated at ambient temperature (20 ± 2ºC). Only batch equilibrium adsorption tests were conducted to investigate whether the local soils would absorb the ammonia nitrogen in the landfill leachate. The idea behind batch equilibrium test is that known quantity of sorbents are mixed with known concentrations of a solution (sorbate) until adsorption equilibrium is reached (Ruthven, 1981). In this study the batch adsorption of ammonia nitrogen removal was investigated in 250 mL bottles (Figure 5-7). For each batch 5.0 g of each dry soil sample was weighed and introduced into each bottle. About 700 ml of landfill leachate sample was adjusted from pH 7.92 (raw leachate pH) to a pH of about 6.0 and then each bottle fed with 100.0 mL of the leachate (Figure 5-7a-c). Hydrochloric acid of 1.0N and pH meter was used to adjust the leachate sample pH.

Previous studies have shown that the optimum conditions for batch adsorption of ammonia nitrogen removal are 50 g/L of sorbent (dry soil) and at a pH value of about 6.0 of sorbate (Haseena, Padmavathy, Krishnan, & Madhu, 2016; Li, Zhao, & Hao, 1999; Vijayakumar, Tamilarasan, & Dharmendirakumar, 2012; Wang et al., 2006). In addition, tests conducted by previous studies confirmed the contact time of 4 hours to be adequate to make ammonia nitrogen concentration reach equilibrium or steady state. Therefore, this study allowed at least 4 hours of contact time for each soil sample. A mechanical stirrer was used to stir the mixture for at least 4 hours as mentioned above (Figure 5-7c). The samples were then allowed to settle for at least 30 minutes and the supernatant solution was carefully drawn and analysed for the remaining ammonia nitrogen (Figure 5-7de). The amount of ammonia nitrogen adsorption (equilibrium adsorption) and ammonia nitrogen percentage removal was estimated using the formulas below:

$$q_e = \frac{(C_o - C_e)V}{(W)} \quad \textbf{(27)}$$

where:

q_e= equilibrium adsorption of ammonium nitrogen adsorption (mg/g)

C_o= initial ammonia nitrogen concentrations (mg/L)

C_e= ammonia nitrogen concentrations at equilibrium (mg/L)

V= volume of leachate solution (L)

W= mass of leachate solution (g)

$$(\%) of\ ammonium\ = \frac{(C_o - C_e)}{(W)} X\ 100 \quad \textbf{(28)}$$

where:

C_o= initial ammonia nitrogen concentrations (mg/L),

C_e= ammonia nitrogen concentrations at equilibrium (mg/L)

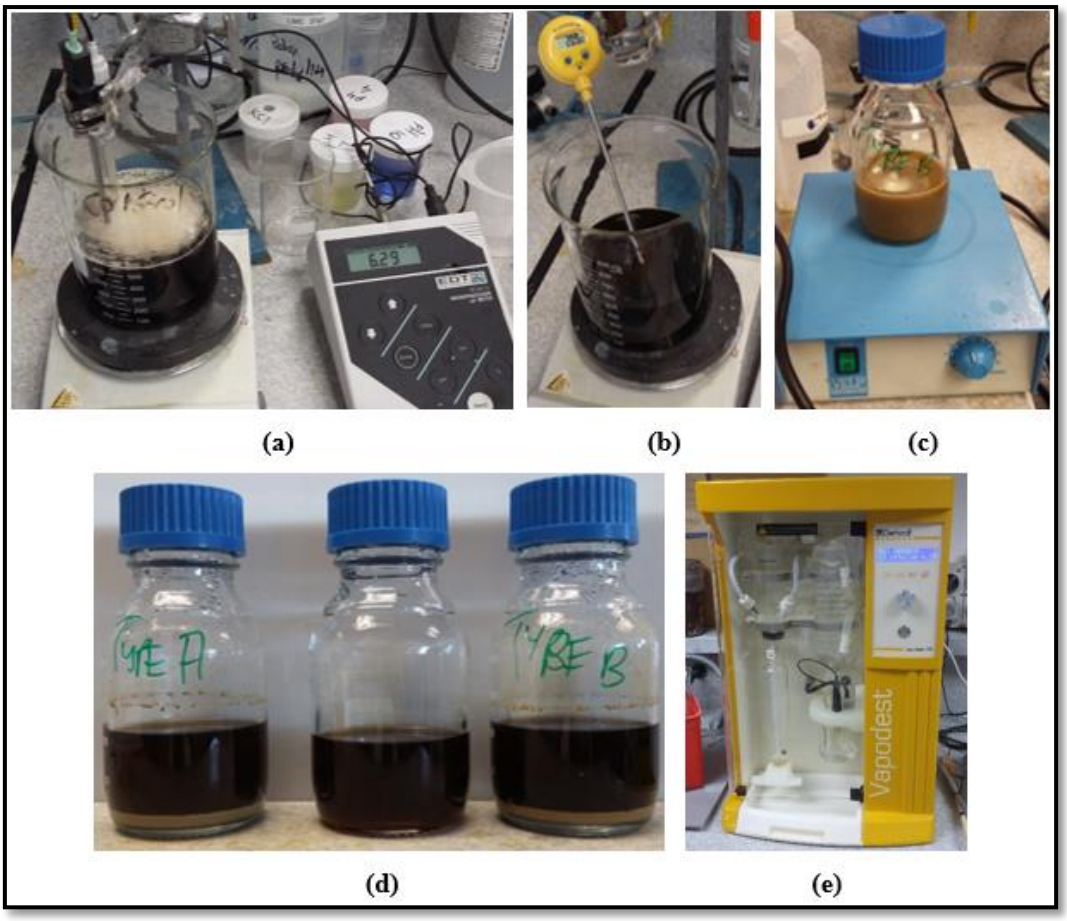


Figure 5-7: (a) Adjusting leachate pH to about 6.0 (b) Leachate ambient temperature kept constant (c) Batch adsorption experiment on soil type B. (d) Sample settling after 8 hours of mechanical stirring. (e) Analysing ammonia nitrogen concentrations using the distillation and titration method.

During the batch adsorption test, visual observations were made including:

- Settling time
- Colour of supernatant

5.3 Results and discussion

5.3.1 Effect of soil type on equilibrium uptake capacity

All the soil samples were analysed for ammonium removal by adsorption. The results are presented in Figure 5-8. The equilibrium ammonium removal capacity was found to be low in soil type A, B and D (1.69, 1.57 and 1.38 mg/g) respectively. It was very low in type C soil achieving only up to 0.26 mg/g. As expected, the equilibrium adsorption of ammonium was

best when using zeolite achieving 9.15 mg/g (raw information in Appendix L). Similar results for equilibrium adsorption of ammonium were achieved by Wang et al., (2006) using zeolites on sewage sludge. He achieved equilibrium uptake capacity of 1.74 mg/g when using natural zeolite on sewage sludge with an initial ammonium concentration of 115.16 mg/L. The high equilibrium adsorption of ammonium with zeolite is due to its high cation exchange properties (CEC). As shown in Figure 5-8 zeolite had a very high CEC of 80 meq/100 g. Previous results by Nguyen and Tanner (1998) found that the higher the cation exchange properties of zeolite, the higher the potential for removing ammonium from wastewaters. On the contrary all the local soils had very low CEC's of less than 6 meq/100, therefore achieving low ammonium removal capacities.

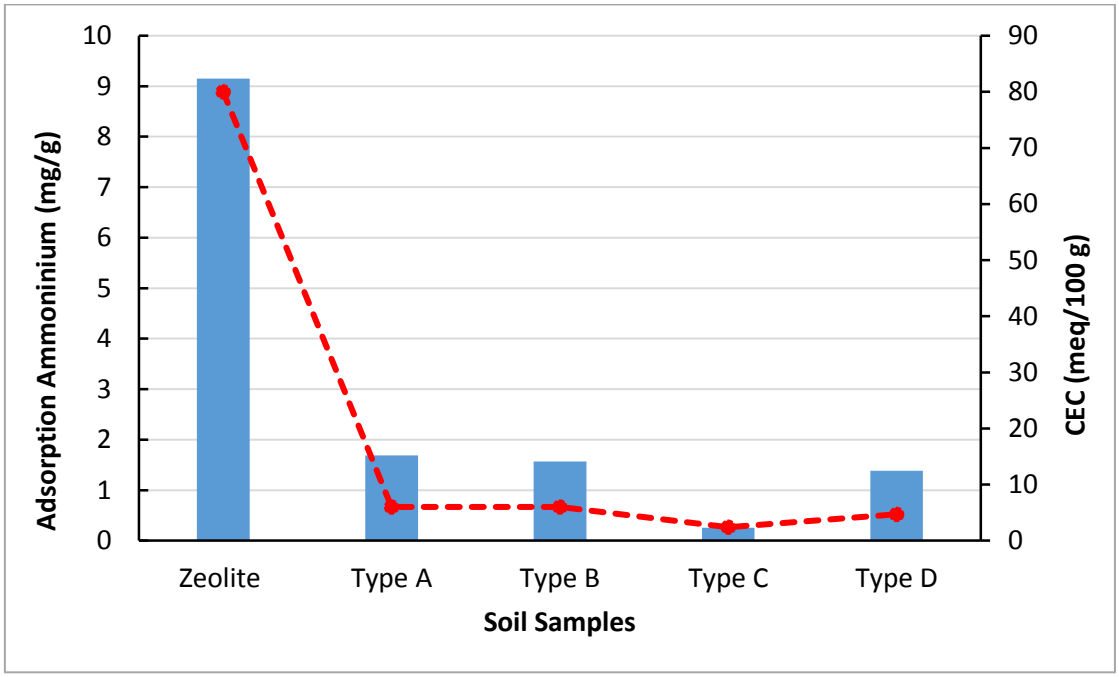


Figure 5-8: Ammonium adsorption rate and CEC for different soils.

5.3.2 Effect of soil type on ammonium removal

The results for percentage ammonium removal using different soils are shown in Figure 5-9. The ammonium removal percentage was found to be low in soil type A, B and D (3.97%, 3.7% and 3.3%) a respectively. It was very low in type C soil achieving only 0.6%. As expected, zeolite achieved high ammonium removal of ~23%. Moreover, similar results were achieved by Wang et al., (2006) using zeolites on sewage sludge. He achieved ammonium removal percentage of ~20% when using natural zeolite on sewage sludge with an initial ammonium concentration of ~115 - 119 mg/L. High ammonium removal with zeolite is due to its high

cation exchange properties and also its clay content as indicated by previous studies. High cation exchange properties and clay content results in the high affinity for cations, hence high potential for ammonia removal from wastewaters or landfill leachate (Haseena et al., 2016; Karadag et al., 2008; Nguyen & Tanner, 1998; Wang et al., 2006). More information of these experiments is presented in first batch results in Appendix L.

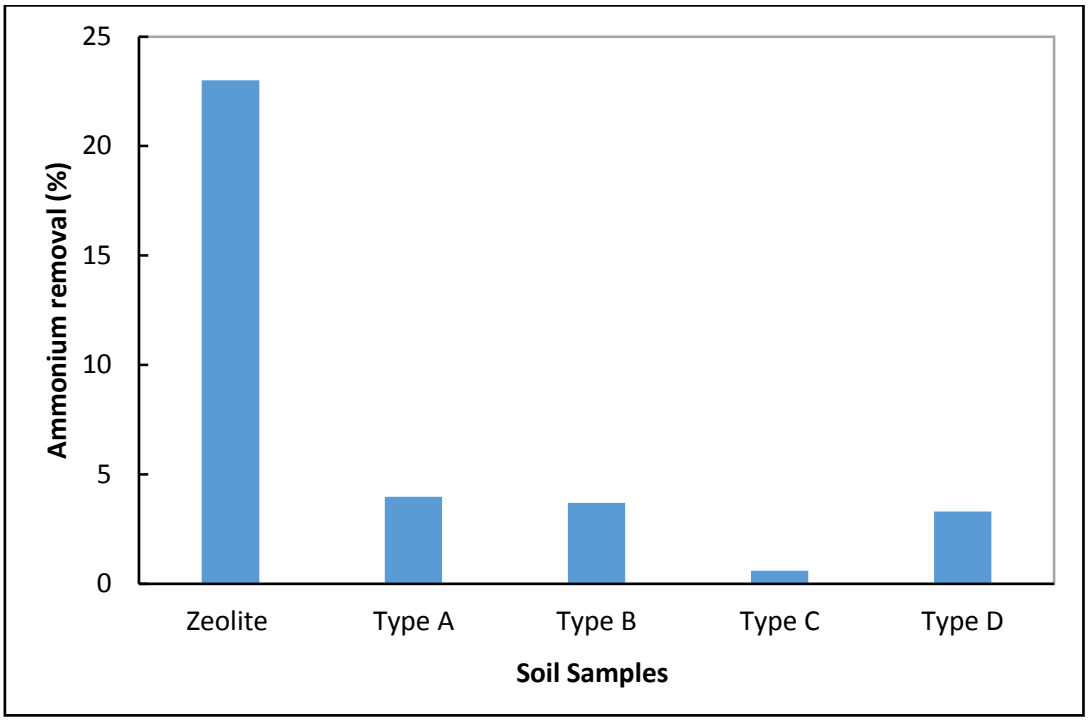


Figure 5-9: Percentage ammonium removal from landfill leachate using different soils.

5.3.3 Effect of clay and silt content on ammonium removal

The variation in ammonium removal with clay and silt content using different soils is shown in Figure 5-10 and Figure 5-11. The ammonium removal percentage was found to be high in soil samples with high clay content and lower in soil with low clay content as shown in Figure 5-10. Zeolite had clay content of 40% with ammonia removal of ~23%. Soil types A, B and D had clay/silt contents of 15%, 13% and 17% respectively hence achieving ammonium removal in the range of 3.0% to 4.0%. On the other hand, type C soil had only 7.0% clay content and achieved only 0.6% of ammonium removal. Figure 5-11 shows the silt content of the soil samples. Two soils (Zeolite and type A) had high silt contents of 51% each but with different clay contents and ammonium adsorption. Zeolite achieved high (23%) ammonium adsorption while type A achieved very low (4.0%) with the same silt content. This shows that ammonium removal performance of soils depended on the clay content not silt content. As mentioned elsewhere, high clay content results in high affinity for cations, hence high potential for

ammonia removal from wastewaters or landfill leachate (Haseena et al., 2016; Karadag et al., 2008; Nguyen & Tanner, 1998; Wang et al., 2006). Therefore, clay content is suitable for predicting ammonium adsorption of soils.

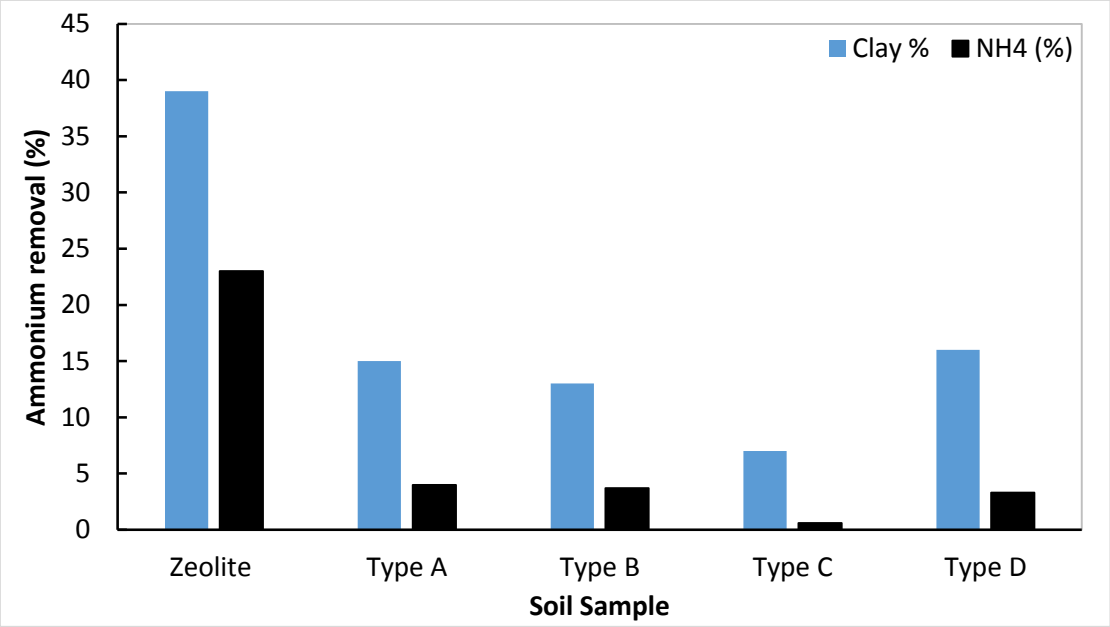


Figure 5-10: Effect of clay on ammonium removal from landfill leachate using different soils.

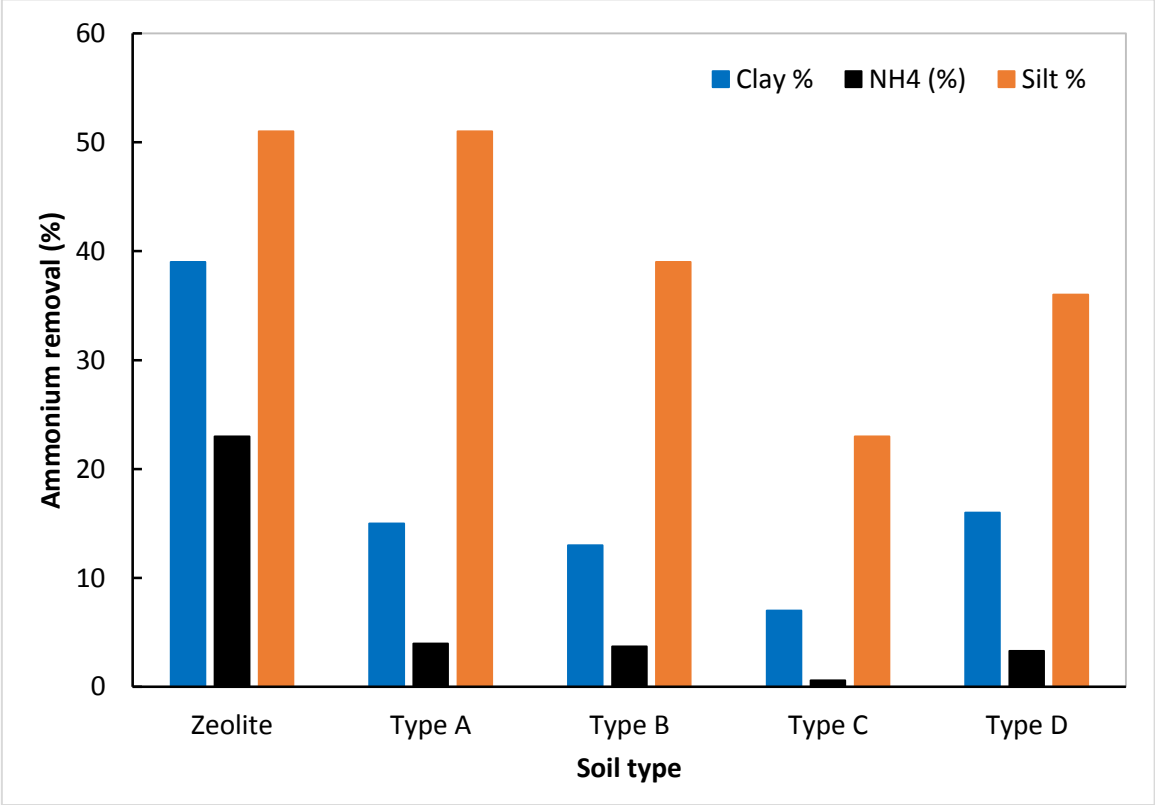


Figure 5-11: Effect of silt on ammonium removal from landfill leachate using different soils.

5.4 Conclusion

This study investigated the potential for removing ammonium from landfill leachate through adsorption using local soils and zeolite. All the four local soils used (type A, B, C and D) were found to be equally ineffective in removing ammonium from landfill leachate. They all achieved less than 5% ammonium removal. However, zeolite was found effective (23%) in removing ammonium from landfill leachate. The ammonium adsorption capacities of the four local soils studied ranged between 0.26 mg/g to 1.7 mg/g while, zeolite achieved ~9.15 mg/g. The ammonium adsorption performance of soils studied depended on clay content and cation exchange properties than silt. The ammonium removal was high in high clay content soils and low in low clay content soils. Zeolite had clay content of 40% with removal of ~23%.

The capacity of the local soils to absorb ammonium could have possibly been inhibited by the presence of competing ions found in the leachates, such as K^+, Na^+, Mg^{2+} and Ca^{2+} (Haseena et al., 2016; Karadag et al., 2008; Nguyen & Tanner, 1998; Wang et al., 2006). Moreover, lower clay content and the presence of organic matter could have had a negative effect on the capacity to remove ammonium by the four local soils. The practicality of using zeolite as a sorbent to remove ammonium from landfill leachate depends entirely on the cost to obtain it. Therefore, its commercial viability may not be very feasible for use in treating ammonium through an adsorption method.

CHAPTER 6. System integration of coagulation–flocculation with biological nitrification: Option 3

This chapter explores the role biological nitrification (with or without coagulation–flocculation) might have in removing ammonia nitrogen from landfill leachate. As indicated in Chapter 4, treatment through coagulation–flocculation only reduced the ammonia nitrogen concentration by around 20% (from 2,260 mg/L to 1,800 mg/L). This leachate still contains very high ammonia nitrogen concentrations, not friendly to the environment or wastewater treatment processes and therefore very toxic to aquatic life in the receiving water bodies. To reduce this concentration further, a biological method was thought to be necessary. As mentioned before, van Loosdrecht et al. (2016) highlighted that the choice of a biological methods depend on the COD/N ratio of the wastewater. Therefore, in this study the average COD is about 4,300 mg/L and TKN is about 2,230 mg/L, which results in a COD/N ratio of about 2 g COD/g N. This falls in the band with COD/N ratio of less than 5 g COD/g N, hence making the nitrification method the biological treatment option worthy of study.

This study investigated the integrated system of coagulation–flocculation (which obtained high COD removal results from experiments with hexahydrate ferric chloride) with a biological nitrification method. The removal of ammonia nitrogen through the nitrification method was assessed, monitored and controlled through sequencing batch activity tests that are discussed below.

6.1 Materials and methods

6.1.1 Activated sludge sample collection and preparation

Nitrification is a biological process whereby ammonium is converted to nitrate by a specialised group of aerobic bacteria (Mihelcic & Zimmerman, 2013; van Loosdrecht et al., 2016). This group of bacteria are called *Nitrosomonas* and *Nitrobacter*. One of the sources of these bacteria is the activated sludge, which was collected from the wastewater treatment plant by drawing it from the return activated sludge sump. A pump was used to draw the mixed liquor sample into a bucket, which was immediately sealed and transported to the University of Canterbury environmental laboratory and stored at 4 °C while awaiting analysis. Storing the mixed liquor sample at 4 °C created non-aerated conditions to prevent the reduction of sulfate that could result in the production of toxic sulfide (van Loosdrecht et al., 2016). Before analysis, the mixed liquor sample was prepared by washing to remove possible toxic substances in it that

could inhibit the treatment of ammonia nitrogen. The washing process entails repeated settling and resuspension of the mixed liquor sample in water at room temperature (at least three times). Figure 6-1 shows the mixed liquor sample washing processes.

Figure 6-1: (a) Activated sludge sample sealed. (b) Settling mixed liquor sample during washing process. (c) Re-suspending the mixed liquor sample during washing process.

6.1.2 Substrate

The performance of the integration system of coagulation–flocculation with biological nitrification in treating ammonia nitrogen was investigated on leachate supernatants (substrate) from experiments with hexahydrate ferric chloride only. These experiments were selected based on COD removal performance obtained with hexahydrate ferric chloride. As shown in Figure 4-15 (Chapter 4), experiments with hexahydrate ferric chloride at a dose of 5,000 mg/L yielded the highest COD removal of 26%, while a dose of 4,200 mg/L achieved COD removal of 25%. Therefore, for logic and cost reasons this study selected substrate from experiments with hexahydrate ferric chloride at a dose of 4,200 mg/L that achieved COD removal of 25% for nitrification processes. The initial concentrations (COD, ammonium, pH, conductivity and turbidity) of the substrate was recorded for further analysis.

6.2 Experimental method

6.2.1 Sequencing batch test experiment - Nitrification batch activity tests

The ammonium removal performance of the nitrification method was tracked through sequencing batch activity tests. Figure 6-2 shows the system integration schematic diagram. The process (chemical tracking) measured ammonium and nitrates concentrations over time. In addition, other parameters of interest assessed over time included COD, DO, pH, conductivity, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). All the analytical procedures followed the common detailed protocols standard methods (APHA et al., 2005) as detailed in Chapter 3. Two batches of experiments were conducted using sequencing batch reactors (SBR): first and second batch experiments.

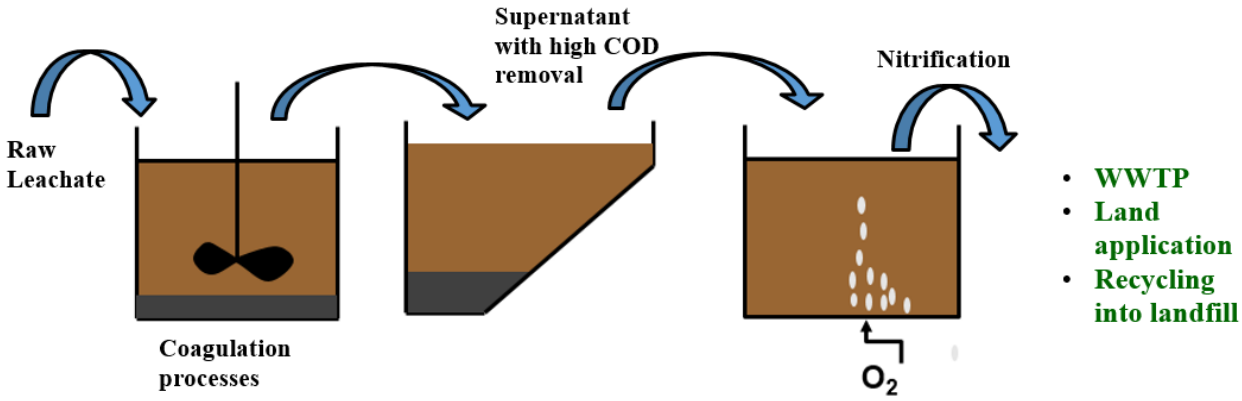


Figure 6-2: Integrated system set-up between coagulation–flocculation processes and nitrification processes.

6.2.1.1 First batch experiments

On the first batch experiments a total sample volume of 1,000 mL was used in a 2.0 L reactor (beaker) volume. The initial MLSS was measured and found to be about 8,000 mg/L. In the first feed about 500 mL (4,000 mg/L MLSS) of mixed liquor sample was transferred into a 2.0 L beaker and 100 ml of substrate (coagulation-treated leachate) was added. A volume of water (400 mL) was also added to make it up to 1,000 mL of total sample volume. (In batch scale experiments, ammonium and COD leachate concentrations were diluted by a factor of 0.1). The solution was mixed with a magnetic stirrer and oxygen was supplied with an aeration system (Figure 6-3). Dissolved oxygen (DO) concentrations of not less than 0.5 mg/L were maintained to avoid it limiting the nitrification processes. Figure 6-3 shows the first batch set-up. These experiments were conducted for 38 consecutive days at different feeds. Samples were taken daily prior to settling before and after each feed. Before the next feed, the mixed

solution was allowed to settle, and then decanted in preparation for the next feed. The sample was analysed for ammonium, nitrates, COD, MLSS and MLVSS. The first feed schedule is presented in Table 6-1.

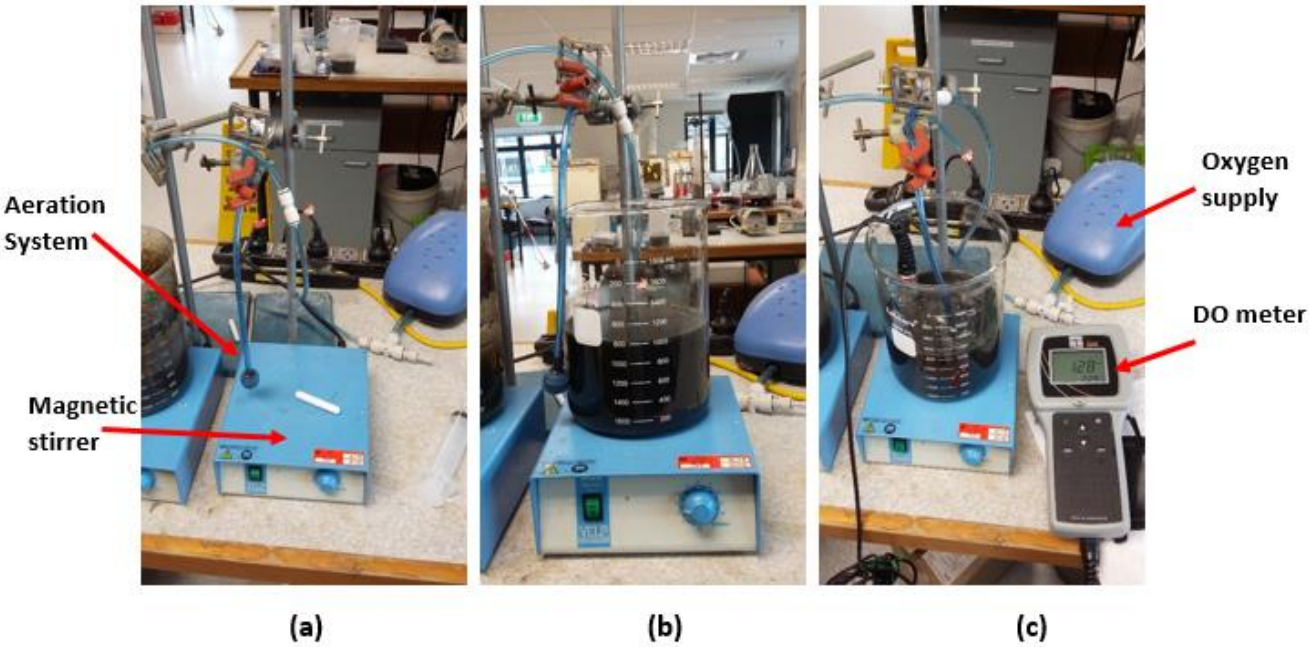


Figure 6-3: First batch set-up. (b) Total sample volume of 1,000 mL.

Table 6-1: Feed 1 Schedule.

FEED 1		
Date	Started 08/09/2016	
Description	Nitrification test at about 20 °C with activated sludge	
Substrate	Pretreated landfill leachate	
Total sampling volume	1,000 mL	
	500 mL	Activated sludge (4,000 mg/L MLSS)
	400 mL	Water
	100 mL	Leachate supernatant (ammonium concentration 50 mg/L; COD 320 mg/L)
Mixed volume initial concentration	200 mg/L	Solution ammonium concentration
	1,019 mg/L	Total COD concentration of the solution
Reactor volume	2.0 L	

6.2.1.2 Second batch experiments

The second batch experiments were conducted slightly differently from the first batch experiments. In these experiments a total sample volume of 2,000 mL was used in a 2.0 L reactor (beaker) volume. The initial mixed liquor sample was measured for MLSS and found to be about 9,200 mg/L. In the first feed, about 1,000 mL (5,270 mg/L MLSS) of mixed liquor

sample and 1,000 mL volume of water was transferred into a 2.0 L beaker. No substrate (coagulated leachate) was added in the first feed. These were allowed to run biologically for a while in order for the bacteria to reduce the activated sludge ammonium and COD in the solution. Two different experiments were conducted at different feeds as shown in Figure 6-4. One experiment was conducted on a substrate from coagulation–flocculation and the other substrate was from raw leachate. In batch scale experiments, ammonium and COD leachate concentrations were diluted by a factor of 0.1. These experiments were conducted for 31 consecutive days at different feeds. Sampling was undertaken every two to four days, before and after each feed, and analysed for ammonium, nitrates, COD, MLSS and MLVSS. In addition, the concentrations of DO, pH and conductivity were monitored closely. More raw data is in Appendix N.

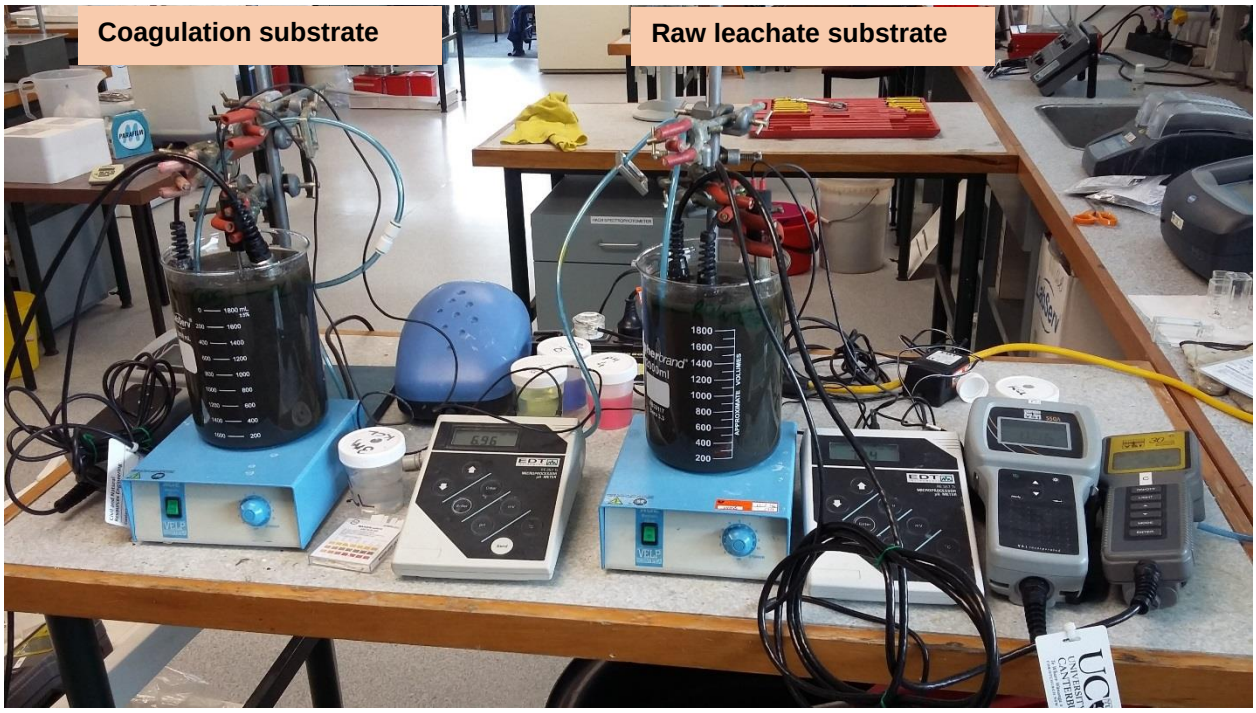


Figure 6-4: Second batch complete set-up.

6.3 Results and discussion

6.3.1 First batch experiments

These experiments were conducted for 38 consecutive days at different feeds as shown in Figure 6-5. Samples were taken daily prior to settling, before and after each feed, and analysed for ammonium, nitrates, COD, MLSS and MLVSS. The removal efficiencies of these

parameters were calculated from characteristics of the influent and effluent of the SBR. Even after washing the mixed liquor sample prior to the nitrification test, high concentrations of COD (1,019 mg/L) in the solution were observed on Day 1, as shown in Figure 6-5. The initial COD concentrations of the substrate before dilution was 320 mg/L. As shown in Figure 6-5 the initial phase of the nitrification test from Day 1 to Day 11 was characterised by a reduction in COD concentrations. During this time, the removal of COD was very high, achieving 98% reduction in COD. During the phase from Day 1 to Day 9, the removal of ammonia was very low (3.0%) while nitrate concentration varied from 1.85 to 7.90 $mgNL^{-1}$. The phase between Day 11 to Day 23 resembles an acclimatisation phase whereby the nitrifying bacteria were starting to utilise the dissolved oxygen to convert ammonia to nitrate. In this phase an average ammonium removal of 46% was achieved, while a nitrate increased from 12 to 22 $mgNL^{-1}$. At Day 23 the concentration of ammonium of the feed was increased from 50 mg/L to 100 mg/L. The idea behind this was to motivate the growth of nitrifying bacteria by feeding them more ammonium. Unfortunately, this increase created an inhibitory environment for the bacteria to convert ammonia to nitrate.

As shown clearly in Figure 6-5, there was a constant increase in ammonium concentrations from Day 23 to Day 38, whereas the nitrate production was variable. An increase in COD concentration was also observed in the solution from Day 13 to Day 31. This could be because of the inhibitory phase created by increasing the ammonium and COD concentration of the feeds. There must also have been some analytical interferences. As shown in Table 6-2, there was a decline in both the MLSS and the bacteria population (MLVSS) throughout the test. This decline could be because of the high concentrations of ammonium and COD in the solution, other inhibitory substances such as heavy metals or a very slow growth of the nitrifying microbes. In view of these issues, the first batch of experiments were stopped.

Table 6-2: MLSS and MLVSS Concentrations from First Batch Experiments.

Sampling time	**No.**	**MLSS** (mg/L)	**MLVSS** (mg/L)
Pre-feed	1	755	705
	2	430	412
	3	280	275
	4	140	125
	Average	401	379
Post-feed	1	710	689
	2	420	410
	3	275	200
	4	127	100
	Average	383	350

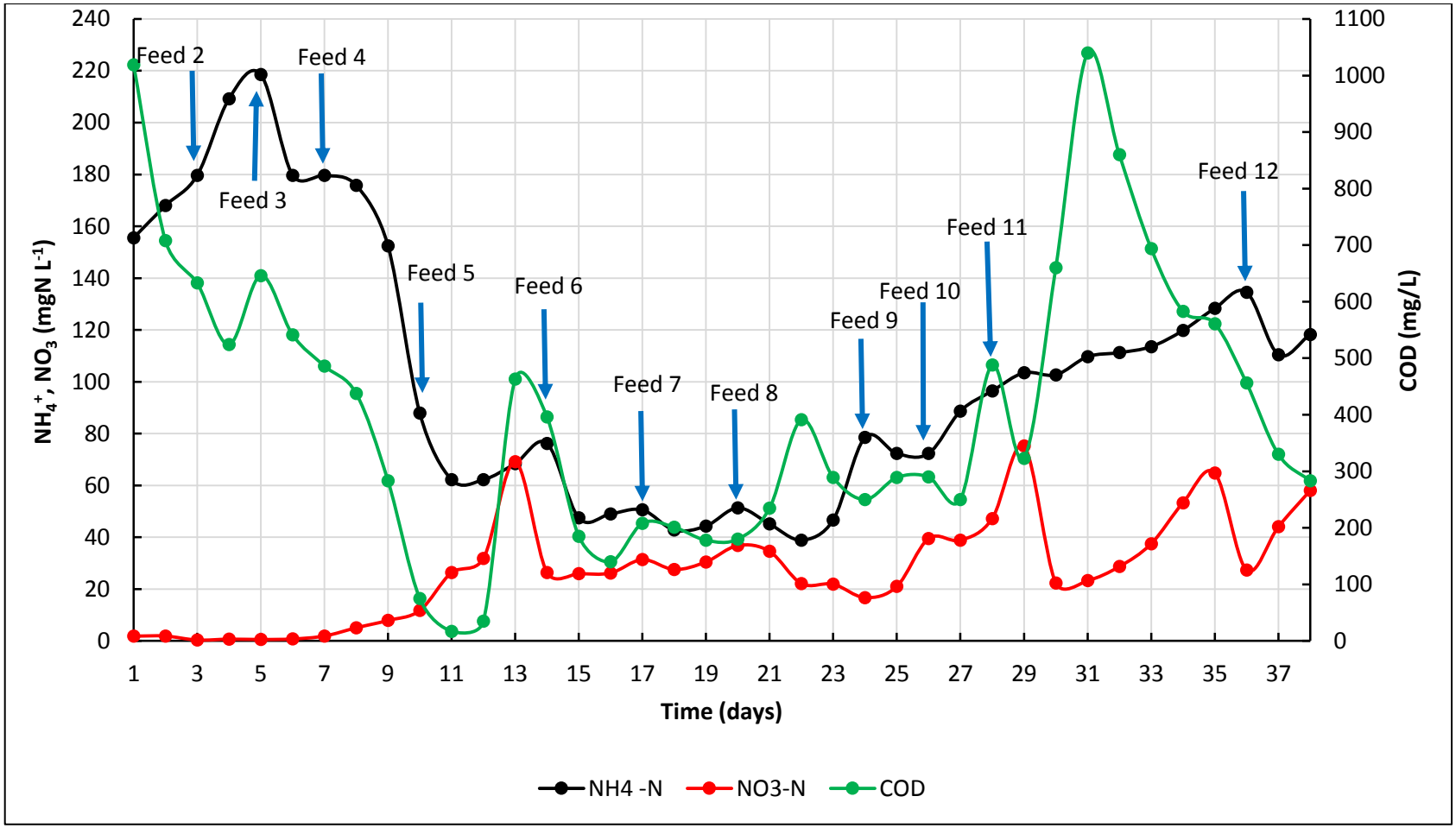


Figure 6-5: Ammonium, nitrate and COD concentrations as obtained from nitrification sequencing batch activity test from first batch experiments.

128

6.3.2 Second batch experiments

The second batch experiments were conducted for 31 consecutive days with different feeding regimes as shown in in Figure 6-6 and Figure 6-7. R1 experiments were conducted on coagulation-treated leachate while R2 experiments were conducted on raw leachate. The reason for these two different substrates was to assess and compare the efficiency of the nitrification treatment on the two substrates. Sampling was undertaken every two to four days after settling, before and after each feed, and then analysed for ammonium, nitrates, COD, MLSS and MLVSS. In addition, the concentrations of DO, pH and conductivity were monitored closely. As in the first batch experiments, the removal efficiencies of these parameters were calculated from the characteristics of the influent and effluent of the SBR. In both R1 and R2, the concentration of ammonium in the feed was kept constant at 50 mg/L.

In the R1 experiments, the initial COD concentration of the solution was 110 mg/L and was reduced by 4% in the first phase (Day 1 to Day 7), as shown in Figure 6-6. The concentration of COD shows a significant, increasing trend across the entire experiment. A similar pattern is observed in the ammonium and nitrate concentrations. However, a significant reduction in ammonium concentrations and nitrates production was observed at each successive feed. For example, at Feed 1 the ammonium concentration was 64.0 mg/L and was reduced by 36.0% before Feed 2. At Feed 2 the ammonium concentration was 102 mg/L and was reduced by 41.0% before Feed 3. Moreover, at Feed 1 nitrate concentration was 65.0 mg/L and was increased to 144 mg/L before Feed 2. At Feed 2 nitrate concentration was 116 mg/L and was increased to 194 mg/L before Feed 3. A similar pattern of COD, ammonium and nitrate performance was also observed on the R2 experiments, and this is shown in Figure 6-7.

During these two experiments a repeated extreme reduction of pH levels (to pH 5.06) of the solution and an increase in conductivity (to 3,250 mS/cm) of the solution was observed. However, this study made repeated attempts to manually control the solution pH by adjusting it to desirable levels every time it dropped, by using sodium hydroxide. Generally, the nitrification process produces acid, which then lowers the pH level of the biological population, hence inhibiting the nitrification process (van Loosdrecht et al., 2016). The decrease in pH level of the biological population resulted in the reduction of nitrifiers (MLVSS), as shown in Table 6-3. The decrease of nitrifiers impacted negatively on the performance of ammonium removal throughout the nitrification process. A summary of the results of the second batch

experiments are presented in Table 6-4. Raw data for these experiments is presented in Appendix M and N.

Table 6-3: MLSS and MLVSS Concentrations from the Second Batch Experiments.

Batch Reactor 1				**Batch Reactor 2**			
Sampling time	**No**	**MLSS** (mg/L)	**MLVSS** (mg/L)	**Sampling time**	**No**	**MLSS** (mg/L)	**MLVSS** (mg/L)
Post-feed	1	5,420	3,510	Post-feed	1	5,420	3,510
	2	1,406	1,260		2	1,326	1,180
	3	1,086	940		3	1,166	1,020
	4	1,000	920		4	1,420	1,340
	5	650	590		5	540	500
	Average	1,912	1,444		**Average**	1,974	1,510
Pre-feed	1	2,666	2,490	Pre-feed	1	2,626	2,370
	2	1,086	940		2	786	640
	3	1,260	1,180		3	1,400	1,340
	4	705	520		4	600	570
	5	450	395		5	490	466
	Average	1,233	1,105		**Average**	1,180	1,077

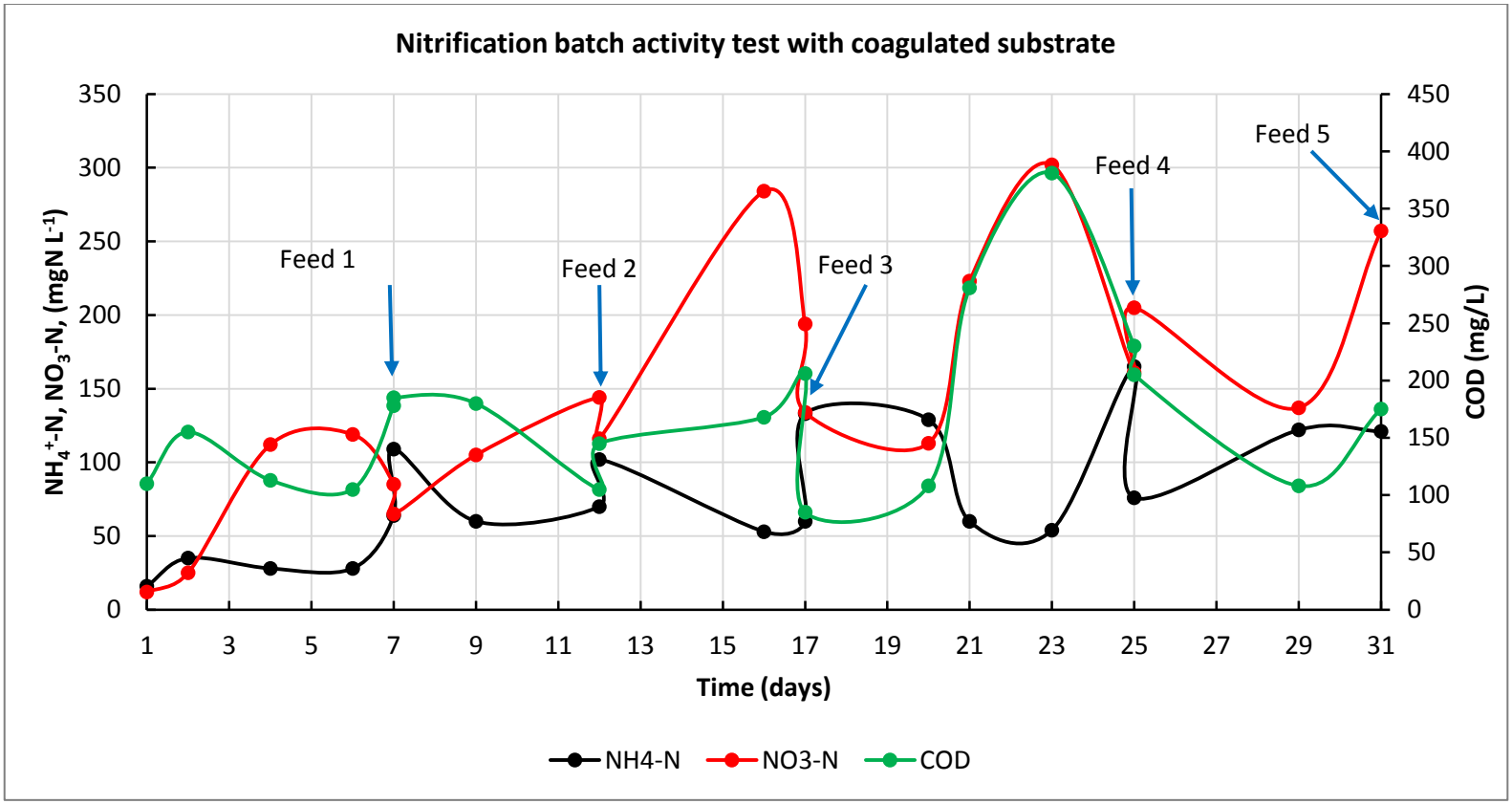


Figure 6-6: Ammonium, nitrate and COD concentrations as obtained from nitrification R1 sequencing batch activity test from first batch experiments.

131

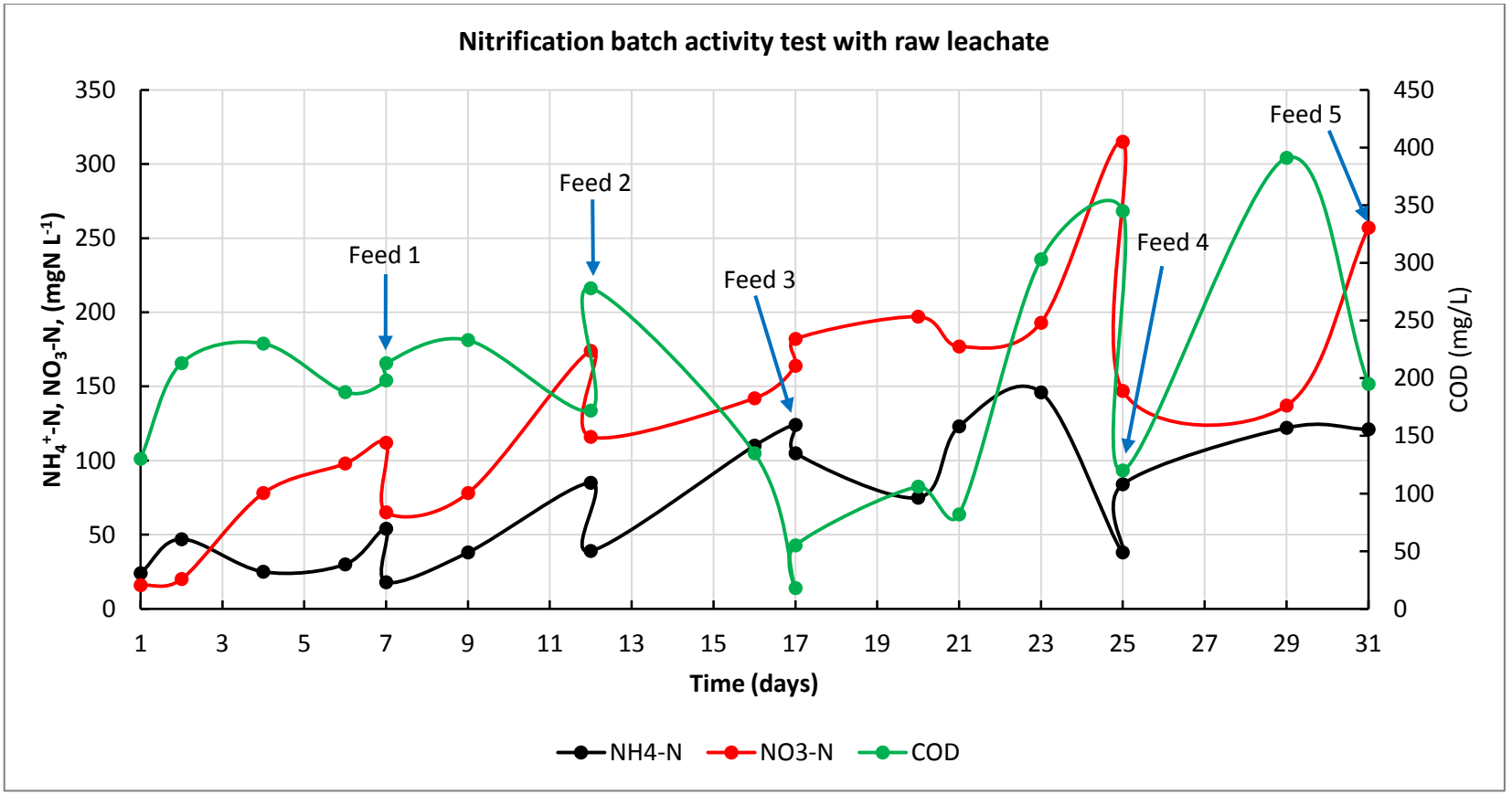


Figure 6-7: Ammonium, nitrate and COD concentrations as obtained from nitrification R2 sequencing batch activity test from first batch experiments.

132

Table 6-4: Summary Results of Second Batch Experiments.

Day	Time (days)	Batch Reactor 1			Batch Reactor 2		
		NH_4-N ($mgNL^{-1}$)	**NO_3-N** ($mgNL^{-1}$)	**COD** (mg/L)	**NH_4-N** ($mgNL^{-1}$)	**NO_3-N** ($mgNL^{-1}$)	**COD** (mg/L)
Friday	1	16	12	110	24	16	130
Saturday	2	35	25	155	47	20	213
Monday	4	28	112	113	25	78	230
Wednesday	6	28	119	105	30	98	188
Friday	7	64	85	178	54	112	198
Friday	7	109	65	185	18	65	213
Sunday	9	60	105	180	38	78	233
Wednesday	12	70	144	105	85	174	172
Wednesday	12	102	116	145	39	116	278
Sunday	16	53	284	168	110	142	135
Monday	17	60	194	206	124	164	18
Monday	17	133	134	85	105	182	55
Thursday	20	129	113	108	75	197	106
Friday	21	60	223	281	123	177	82
Sunday	23	54	302	381	146	193	303
Tuesday	25	165	161	230	38	315	345
Tuesday	25	76	205	205	84	147	120
Saturday	29	122	137	108	122	137	391
Monday	31	121	257	175	121	257	195

6.4 Conclusion

This study explored the potential of a method for removing ammonium from landfill leachate through the combination of coagulation–flocculation and biological nitrification processes. The preliminary trial performance of this integrated system was investigated using SBR on leachate supernatants (substrate). The substrate used was from experiments conducted with hexahydrate ferric chloride, which obtained high COD removals. Two batches of experiments were conducted: the first batch was conducted for 38 consecutive days while the second batch was conducted for 31 days. In the first batch experiments, high COD removal of 98% was obtained between Day 1 and Day 11 of the nitrification test phase. During this phase, from Day 1 to Day 9, the average removal of ammonia was very low (3.0%) while nitrate production was from 1.85 to 7.90 $mgNL^{-1}$. High ammonium removal average (46%) was achieved in the phase between Day 11 and Day 23, while nitrate production increased from 12 to 22 $mgNL^{-1}$. A constant volume of substrate feed containing 50 mg/L of ammonium was maintained from Day

1 to Day 23. Thereafter, the feed volume was increased to give an ammonium concentration of 100 $mgNL^{-1}$. It is this increase of the feed volume and ammonium concentration that led to the reduction in the biological population and also to an increase in ammonium concentration in the solution. From Day 23 to the end there was no more ammonium removal, which led to the termination of this experiment.

Second batch experiments were conducted on different substrates (R1 and R2). R1 experiments were conducted on coagulated leachate substrates while R2 experiments were conducted on raw leachate. In both R1 and R2, the concentration of ammonium of the feed was kept constant at 50 $mgNL^{-1}$ in all the feeds. Generally, in these two experiments a significant reduction of ammonium concentration and nitrate production was observed at each successive feed. For example, at Feed 1 (R1) the ammonium concentration was 64.0 $mgNL^{-1}$ and was reduced by 36.0% before Feed 2. At Feed 2 the ammonium concentration was 102 $mgNL^{-1}$ and was reduced by 41.0% before Feed 3. Moreover, at Feed 1 the nitrate concentration was 65.0 $mgNL^{-1}$and was increased to 144 $mgNL^{-1}$ before Feed 2. At Feed 2 nitrate concentration was 116 $mgNL^{-1}$ and was increased to 194 $mgNL^{-1}$ before Feed 3. However, in these two experiments a significant trend of increasing ammonium, nitrate and COD concentrations over the entire experiments was observed.

Generally, the combination of coagulation–flocculation and biological nitrification processes did not perform satisfactorily in this study. Some of the possible reasons for this poor performance could be because the diluted leachate used as a substrate still contained very high ammonium and COD concentrations that proved to be toxic to the biological population. Secondly, the SBR in these experiments were operated manually, which proved very challenging when attempting to control pH levels, DO, conductivity and temperature of the solution. A repeated pH reduction of the biological population was observed. According to literature, pH levels outside the range from 7.5 to 8.5 inhibit the nitrification processes, and pH levels of 5.06 were observed repeatedly during this experiments. Moreover, DO levels of less than 0.5 mg/L were observed repeatedly, which could have impacted negatively on the nitrification processes.

CHAPTER 7. System integration of adsorption with coagulation–flocculation: Option 4

This chapter discusses the system integration between adsorption and the coagulation–flocculation method to remove ammonia nitrogen from landfill leachate. As indicated in Chapter 5, treatment through adsorption was investigated on five soils. Four of the soils investigated were local soils (type A, B, C and D) collected from a local landfill site, while one soil was zeolite sourced from a quarry in New Zealand. The four local soils were found to be equally ineffective in removing ammonium from landfill leachate, achieving less than 5% ammonium removal. Zeolite was found to be more effective in removing ammonium from landfill leachate, achieving about 23% ammonium removal. Therefore, in view of these results, this study investigated the potential for further removing ammonium from landfill leachate by integrating an adsorption method with a coagulation–flocculation method: that is, by first treating the leachate using an adsorption method and then further treating the treated leachate (decanted material) using coagulation–flocculation. Anhydrous ferric chloride and aluminium sulfate were also used as coagulants for the coagulation–flocculation processes.

7.1 Materials and methods

7.1.1 Landfill leachate, zeolite (sorbent) and anhydrous ferric chloride (coagulant)

These experiments used landfill leachate, zeolite soil, anhydrous ferric chloride and aluminium sulfate. Leachate sampling and analysis is discussed in detail in Chapter 3, while the sourcing of zeolite and its characteristics are discussed in Chapter 5. Lastly, sourcing of anhydrous ferric chloride and aluminium sulfate is also discussed in Chapter 4.

7.2 Experimental method

In these experiments the raw landfill leachate was first treated through an adsorption method by using zeolite as the sorbent. These experiments followed the experimental methods in Chapter 5 (5.2). The treated leachate (decanted material) was analysed for ammonia nitrogen, COD, colour and turbidity reductions and then further treated with coagulation–flocculation processes. The coagulants used in these experiments were anhydrous ferric chloride and aluminium sulfate at several doses, ranging from 1,000 mg/L to 3,000 mg/L and from 2,000 mg/L to 8,000 mg/L respectively. The supernatant was then analysed for ammonia nitrogen, COD, colour and turbidity reductions. Moreover, the experimental methods employed in coagulation–flocculation followed the experimental methods in Chapter 4 (4.3.1). Figure 7-1

shows the schematic diagram of the system integrated of adsorption and coagulation–flocculation processes.

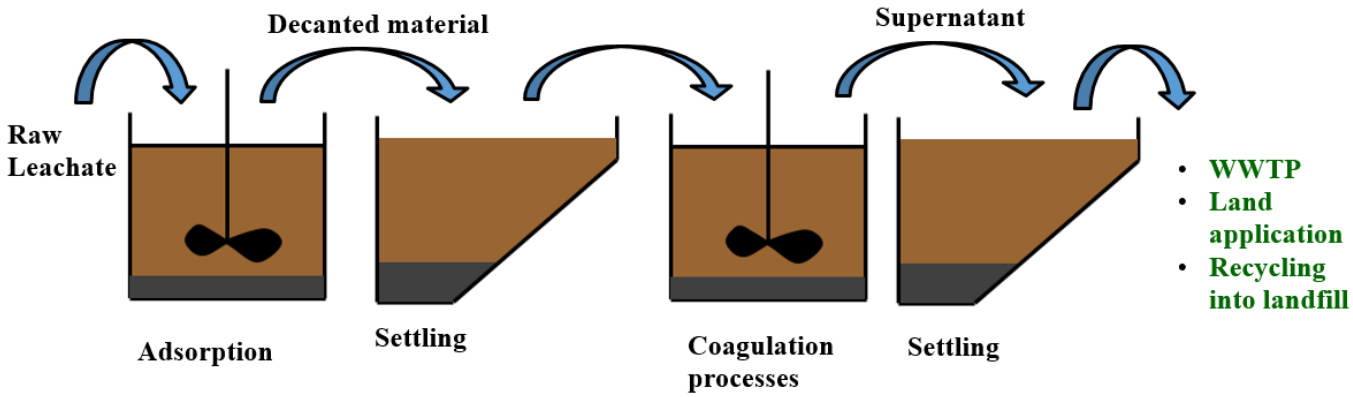


Figure 7-1: Integrated system set-up of the adsorption and coagulation–flocculation processes.

7.3 Results and discussion

7.3.1 First experiments - adsorption

Three leachate samples were first analysed for ammonium removal by adsorption using zeolite soil. Sample B and C are from the same leachate batch while sample A is from a different batch: the results are presented in Figure 7-2 and Figure 7-3. These experiments achieved relatively similar equilibrium ammonium removal capacity. Sample A and C each achieved 10.4 mg/g, while sample B achieved 10.5 mg/g. Similarly, the percentage ammonium removal for samples A, B and C were 24%, 26% and 25% respectively. These results are relatively similar to those in Chapter 5 (23% ammonium removal). Adsorption summary results are presented in Table 7-1 along with pH, COD, colour and turbidity results.

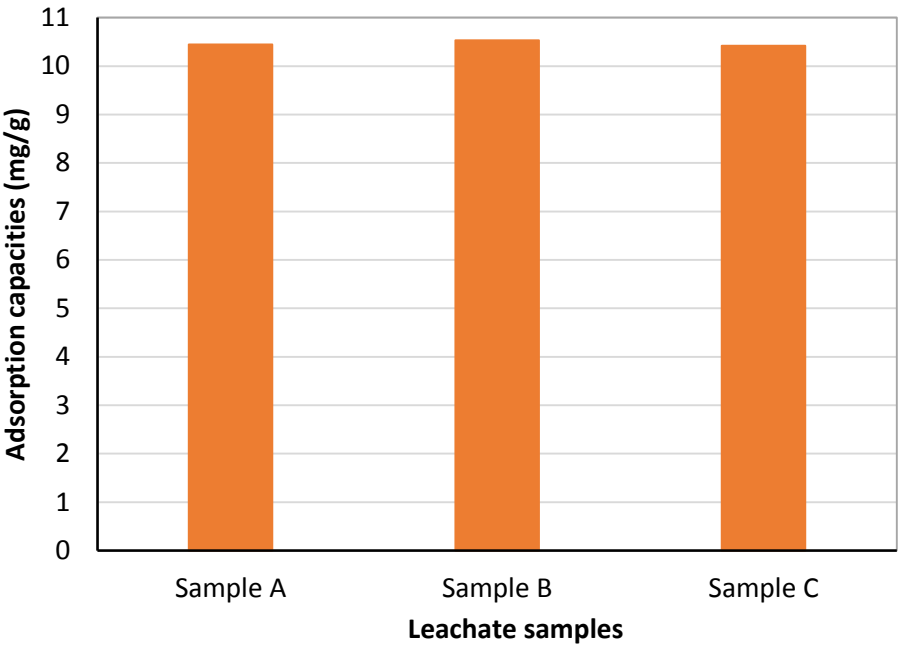


Figure 7-2: Ammonium adsorption rate of landfill leachate samples from different batches.

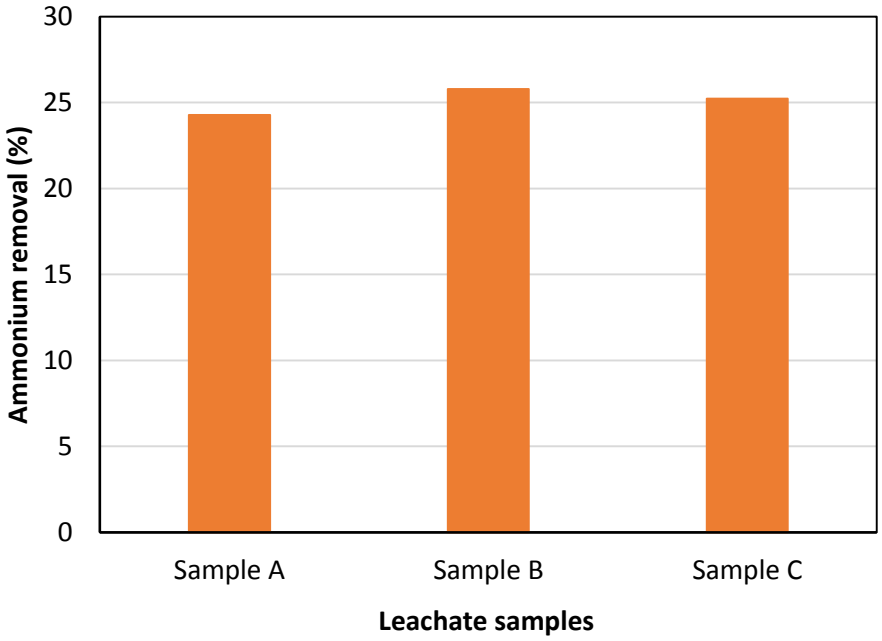


Figure 7-3: Percentage ammonium removal of landfill leachate samples from different batches.

Table 7-1: Adsorption summary results using zeolite (adsorbent) at initial and final pH of 6.0 and 6.5 respectively. The adsorbent dose was 50,000 mg/L, with shaking time and speed of 6.0 hr and 350 to 400 rpm respectively and 90 minutes of settling time.

Sample/ sorbate	**Initial NH_4-N** (mg/L)	**Final NH_4-N** (mg/L)	**NH_4-N adsorption** (mg/g)	**NH_4-N removal** (%)	**COD removal** (%)	**Colour removal** (%)	**Turbidity Increase** (%)
Leachate Sample A	2152	1629	10.4	24.0	11.7	24.0	2.0
Leachate Sample B	2049	1522	10.5	26.0	10.2	24.0	2.0
Leachate Sample C	2065	1544	10.4	25.0	10.2	24.0	2.0

7.3.2 Coagulation–flocculation experiments

The second step of the integration system involved further treating the initially treated leachate (by adsorption) through coagulation–flocculation. The coagulants used in these experiments were anhydrous ferric chloride and aluminium sulfate at several doses. The supernatant was then analysed further for ammonia nitrogen, COD, colour and turbidity reductions.

7.3.2.1 Ammonia nitrogen and COD results

The total ammonia nitrogen results are presented in Figure 7-4: anhydrous ferric chloride was investigated at different sample initial pH levels (pH 6.5 and 7.0). Note that the final concentrations (Table 7-1) of ammonia nitrogen from the adsorption treatment were now used as the initial ammonia nitrogen concentrations of the leachate in the coagulation–flocculation experiments (Figure 7-4). At pH 7.0 the experiments with anhydrous ferric chloride reduced ammonia nitrogen concentrations from 1,521 mg/L to 1,314 mg/L at a dose of 1,500 mg/L, thus a maximum reduction of 14.0%. When comparing to the previous second batch coagulation–flocculation results in Chapter 4 (4.4.2.2), a maximum of 20% (from initial concentration of 2,120 mg/L to 1,686 mg/L) ammonia nitrogen removal was obtained at a dose of 2,000 mg/L, while a dose of 1,500 mg/L achieved only 5.0%. The integration of adsorption with anhydrous ferric chloride at pH 7.0 achieved the highest total ammonia nitrogen removal of 36%.

At pH 6.5 the experiments with anhydrous ferric chloride reduced ammonia nitrogen concentrations from 1,629 mg/L to 1,400 mg/L at a dose of 1,000 mg/L, thus a maximum

reduction of also 14.0%. Therefore, achieving a maximum total ammonia nitrogen removal of 35% when integrating adsorption with anhydrous ferric chloride at pH 6.5. In contrast, at pH 6.5 the experiments with alum on adsorption-treated leachate reduced ammonia nitrogen concentrations from 1,544 mg/L to 1,441 mg/L at a dose of 6,000 mg/L, thus a maximum reduction of about 7.0%. Therefore, achieving the maximum total ammonia nitrogen removal of 30% when integrating adsorption with alum at pH 6.5. In summary, the integration between adsorption and anhydrous ferric chloride performed better than with alum achieving the highest ammonia nitrogen removal (36%) at a lower anhydrous ferric chloride dose of 1,500 mg/L.

The COD reductions were only analysed on experiments with anhydrous ferric chloride at different pH levels as shown in Figure 7-5. At pH 6.5 the experiments with anhydrous ferric chloride on adsorption-treated leachate reduced COD concentrations from 3,344 mg/L to 2,025mg/L at a dose of 1,000 mg/L, thus a maximum reduction of 39.0%. Therefore, achieving the highest total COD removal of 47% when integrating adsorption with anhydrous ferric chloride at pH 6.5. At pH 7.0 the experiments with anhydrous ferric chloride on adsorption-treated leachate reduced COD concentrations from 3,400 mg/L to 2,000 mg/L at a dose of 3,000 mg/L, thus a maximum reduction of 41.0%. In these experiments integrating adsorption with anhydrous ferric chloride at pH 6.5 performed better than with anhydrous ferric chloride at pH 7.0 in COD treatment. The previous COD results in Chapter 4 (4.4.2.2) on coagulation–flocculation with anhydrous ferric chloride at pH 7.0 achieved a maximum of 32% COD (from initial concentration of 4,005 mg/L to 2,780 mg/L) removal at a dose of 5,000 mg/L, while a dose of 3,000 mg/L achieved 28%.

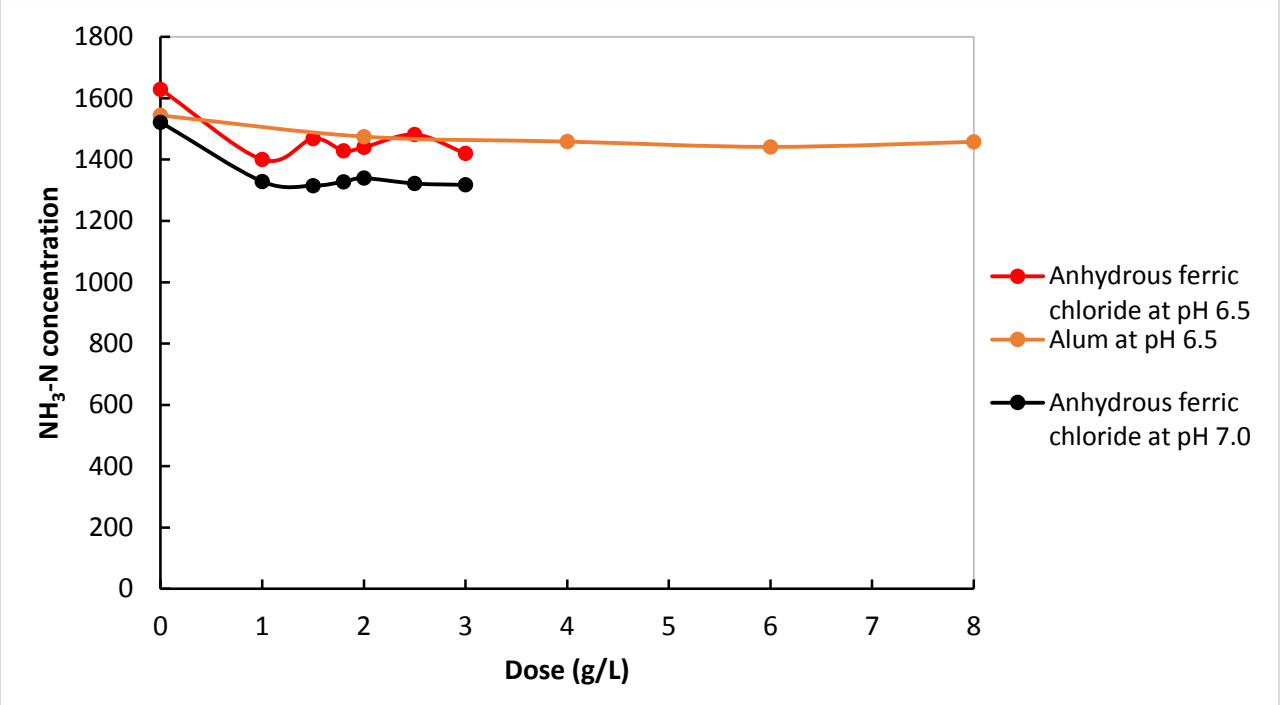


Figure 7-4: Ammonia nitrogen removal results with adsorption-treated leachate for different coagulant types at different pH levels.

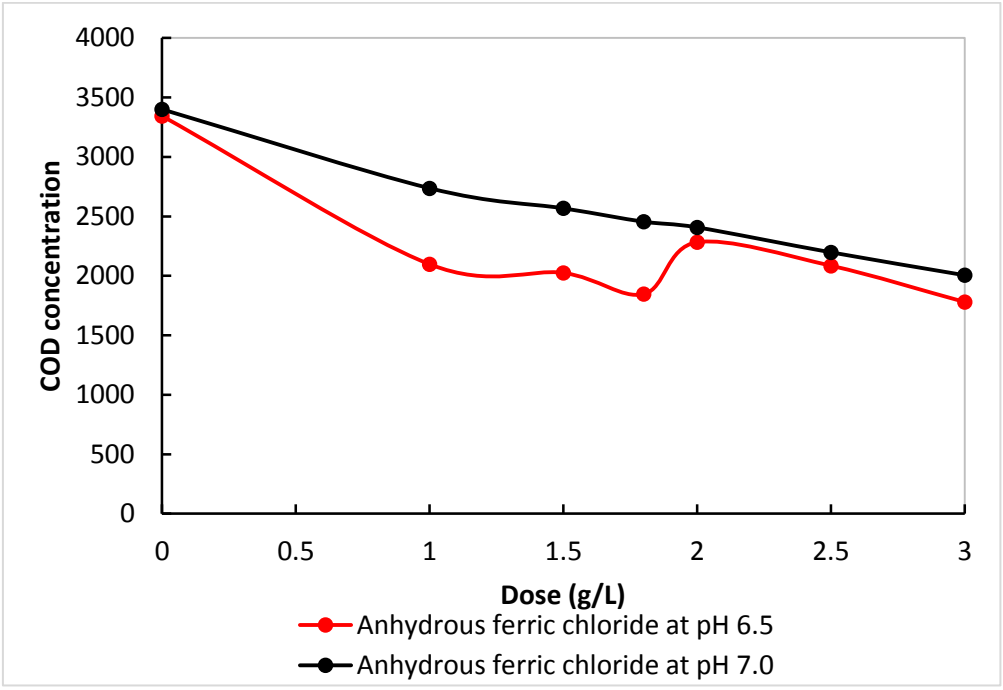


Figure 7-5: COD removal results for adsorption-treated leachate with anhydrous ferric chloride at different pH levels.

7.3.2.2 Colour and turbidity results

Colour and turbidity results are presented in Figure 7-6 and Figure 7-7. As shown in Figure 7-6, a significant colour removal of 24% was obtained with adsorption experiments. An integration between adsorption and anhydrous ferric chloride at pH 6.5 obtained high percentages of colour removal, ranging from 71% to 96% across the doses used. A maximum of 96% colour reduction was achieved at a dose of 3,000 mg/L. Moreover, integration between adsorption and anhydrous ferric chloride at pH 7.0 still obtained high colour reductions, ranging from 61% to 89%. A maximum of 89% colour reduction was achieved, still at a dose of 3,000 mg/L. The previous first batch colour results in Chapter 4 (4.4.2.1) on coagulation–flocculation with anhydrous ferric chloride at pH 7.0 achieved a maximum of 77% colour (from initial concentration of 8,920 PtCo to 2,080 PtCo) removal at a dose of 3,500 mg/L, while a dose of 3,000 mg/L achieved 66%.

Experiments with integrating adsorption with alum obtained colour reductions ranging from 48% to 93% with alum doses ranging from 2,000 mg/L to 12,000 mg/L. An increase in colour reductions with increasing alum dose was observed during experiments with alum. In these experiments, integrating adsorption with anhydrous ferric chloride at pH 6.5 performed better than any other integration in terms of colour treatment.

As shown in Figure 7-7, about 2.0% increase in turbidity was observed with the adsorption experiments. An increase in turbidity removal was observed with increasing coagulant dose concentrations when integrating adsorption with anhydrous ferric chloride at pH 7.0. A maximum turbidity (75%) removal was achieved at a dose of 3,000 mg/L. When integrating adsorption with anhydrous ferric chloride at pH 6.5, an increase in turbidity of 5% at a dose of 1,000 mg/L was initially experienced. Thereafter an increase in turbidity removal was observed with increasing coagulant dose, achieving a maximum of 85% of turbidity removal at a dose of 3,000 mg/L. Therefore, the results of integrating adsorption with anhydrous ferric chloride at pH 6.5 were better than with anhydrous ferric chloride at pH 7.0 in terms of turbidity treatment.

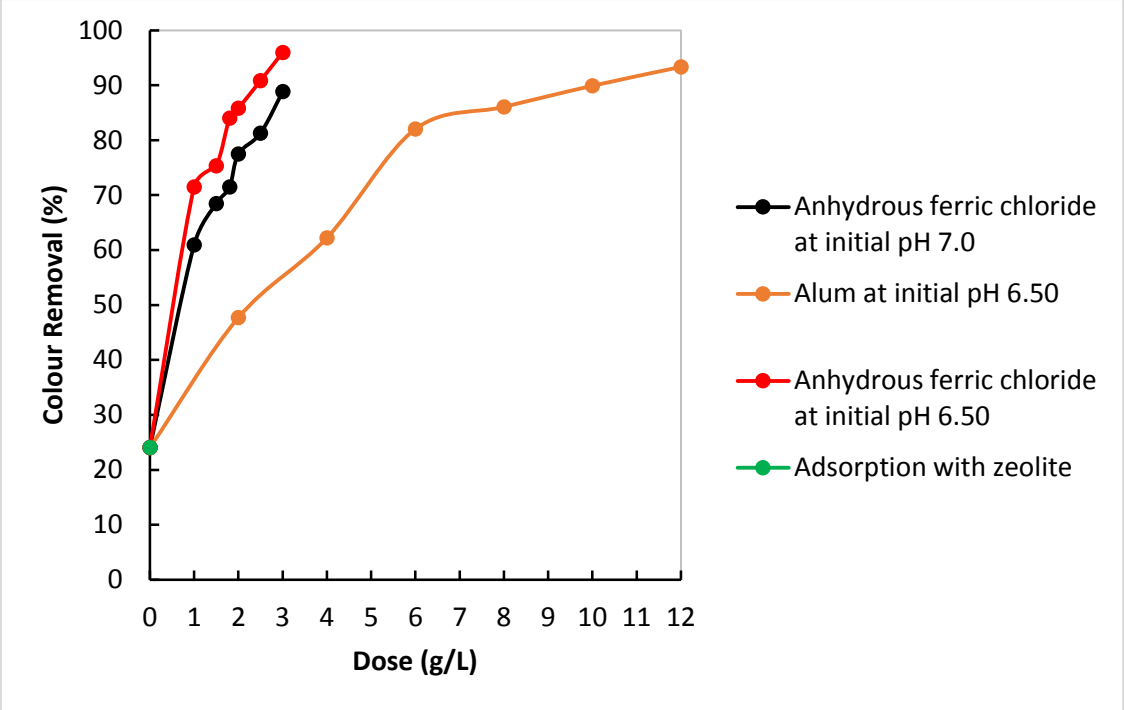


Figure 7-6: Colour removal results with different coagulant types at different pH levels.

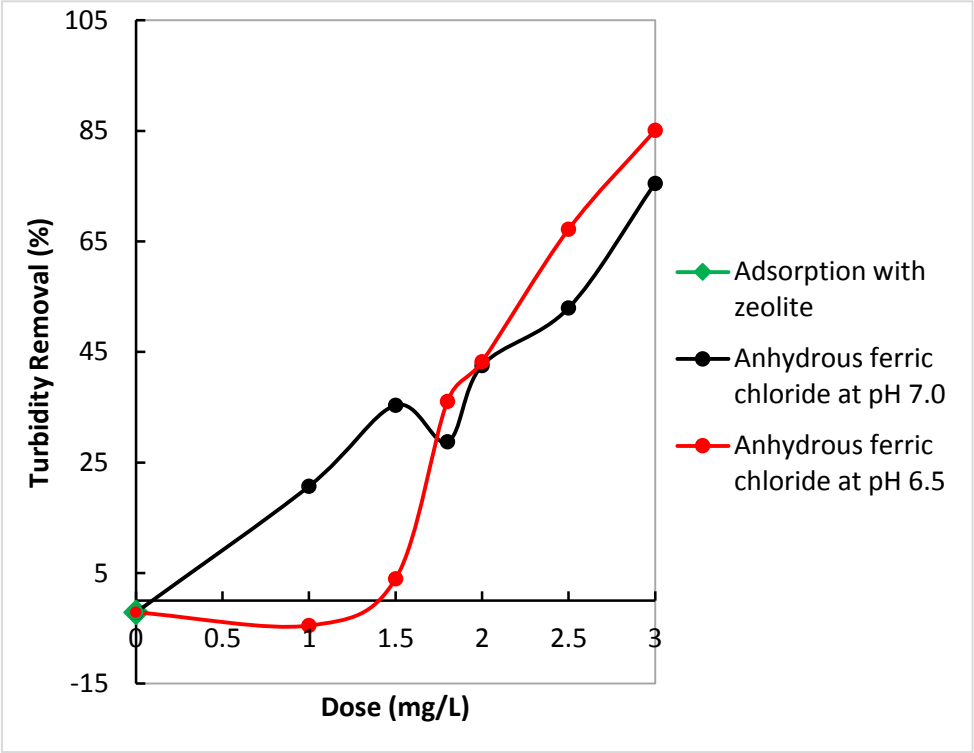


Figure 7-7: Turbidity removal results with anhydrous ferric chloride at different pH levels.

7.4 Conclusion

This study investigated the potential for removing ammonium from landfill leachate by integrating an adsorption method with a coagulation–flocculation method. The performance of this integration was investigated by first treating the leachate using an adsorption method with zeolite soil and then further treating the treated leachate with anhydrous ferric chloride and aluminium sulfate through coagulation–flocculation. The adsorption method achieved an average ammonium removal of about 25%, an average COD removal of 10.7%, 24% colour removal and a 2.0% increase in turbidity concentration. Treating further the adsorption-treated leachate using coagulation–flocculation with anhydrous ferric chloride at pH 7.0 reduced ammonia nitrogen concentrations by 14.0% (from 1,521 mg/L to 1,314 mg/L) at a dose of 1,500 mg/L. Therefore, achieving the highest total ammonia nitrogen removal of 36% when integrating adsorption with anhydrous ferric chloride at pH 7.0. Coagulation–flocculation with alum at pH 6.5 reduced ammonia nitrogen concentrations further by 7.0% making it to a total ammonia nitrogen removal of 30% with the integration system. In summary, the integration between adsorption and anhydrous ferric chloride performed better than with alum achieving the highest ammonia nitrogen removal (36%) at a low coagulant dose of 1,500 mg/L.

A different pattern was observed on COD reductions. Treating further the adsorption-treated leachate using coagulation–flocculation with anhydrous ferric chloride at pH 6.5 and 7.0 reduced COD concentrations by 39% and 41% respectively, thus each achieving a total COD removal of 47% when integrating adsorption. Moreover, experiments integrating adsorption with anhydrous ferric chloride at pH 6.5 performed better in colour treatment. This combination achieved very high colour removal of about 96% at a dose of 3,000 mg/L, while experiments with anhydrous ferric chloride at pH 7.0 obtained high colour reductions of 89% at the same dose of 3,000 mg/L. Experiments that integrated adsorption with alum obtained high (93%) colour reductions, however, at a high dose of 12,000 mg/L. The best turbidity treatment (85%) was also achieved by integrating adsorption with anhydrous ferric chloride at pH 6.5 while anhydrous ferric chloride at pH 7.0 produced about 75% reduction.

Generally, the integration of an adsorption method with coagulation–flocculation improved treatment for ammonia nitrogen, COD, colour and turbidity from landfill leachate, achieving maximum reductions of 36%, 47%, 96% and 85% respectively. However, this treatment still produces landfill leachate with high (1,450 mg/L) ammonia nitrogen concentrations, which is

unsafe to discharge into the environment and also expensive to treat at wastewater treatment plants.

CHAPTER 8. Overall conclusion

8.1 Individual options

This study explored different options for treating ammonia nitrogen from landfill leachate: coagulation–flocculation, adsorption, an integrated system of coagulation–flocculation with biological nitrification, and an integrated system of adsorption and coagulation–flocculation. The leachate samples from this study had average ammonia nitrogen and COD concentrations of 2,260 mg/L and 4,340 mg/L respectively.

The first individual option explored was coagulation–flocculation using anhydrous ferric chloride, hexahydrate ferric chloride and aluminium sulfate as coagulants to remove ammonia nitrogen from landfill leachate. In addition, the effectiveness of three commercial cationic polyelectrolytes (Magnesol 598, Crystalfloc and Magnafloc LT7991) in removing ammonia nitrogen from landfill leachate through coagulation–flocculation was investigated. Among these three coagulants, anhydrous ferric chloride at pH 7.0 was found to be more effective in the treatment of landfill leachate than hexahydrate ferric chloride and aluminium sulfate in achieving 20%, 29% and 77% of ammonia nitrogen, COD and colour removal respectively at a dose of 2,000 mg/L, while aluminium sulfate achieved 15% of ammonia nitrogen removal at pH 7.0 and at a dose of 14,000 mg/L. Moreover, alum achieved high COD and colour reductions of 36% and 88 % at the same dose.

The hexahydrate ferric chloride at pH 7.0 achieved very low ammonia nitrogen removal of 9.0%, and 26% COD reduction at a dose of 3,000 mg/L. Generally, the addition of cationic polyelectrolytes was ineffective, showing a decline in ammonia nitrogen (less than 9.0%) and COD removal. In contrast, the interaction between hexahydrate ferric chloride and Magnesol 598 exhibited a good performance in turbidity removal, achieving a maximum of 94% at a dose of 3,000 mg/L of hexahydrate ferric chloride and 30 ml/L of Magnesol 598.

In summary, using anhydrous ferric chloride for treating ammonia nitrogen from landfill leachate through coagulation–flocculation method reduced ammonia nitrogen from landfill leachate by 20% (from 2,260 mg/L to 1,800 mg/L). This leachate still contains very high ammonia nitrogen concentrations: not friendly to the environment and therefore very toxic to aquatic life in the receiving water bodies. This leachate would still potentially deplete dissolved oxygen and contribute to eutrophication in the surrounding water bodies. This leachate could

still impact negatively on the wastewater treatment processes; hence the landfill owners could still be charged for treating their leachate at wastewater treatment plants. Overall, ammonia nitrogen treatment through coagulation–flocculation alone would still retain all the initial leachate concerns for the environment.

The second individual option explored was adsorption using local soils and zeolite. All the four local soils used (type A, B, C and D) were found to be equally ineffective in removing ammonium from landfill leachate. They all achieved less than 5.0% ammonium removal. In contrast, zeolite was found somewhat effective (23%) in removing ammonium from landfill leachate. However, zeolite might be cost effective (not commercial viable) for use in treating ammonium through an adsorption method. Also, 23% removal resulted in a final ammonium concentration of 1,740 mg/L which is too high because of the reasons above.

8.2 Systems integration

In view of the low ammonia nitrogen treatment results achieved by individual methods (coagulation–flocculation and adsorption), the option of system integration was investigated. Two system integrations were analysed: integration between coagulation–flocculation and biological nitrification, and integration between adsorption and coagulation–flocculation.

The first system integration (third option) explored the potential for removing ammonium from landfill leachate through the combination of coagulation–flocculation and biological nitrification processes. In these experiments, the preliminary trial performance of this system integration was analysed using a sequencing batch reactor on leachate supernatants from experiments conducted with hexahydrate ferric chloride (which obtained high COD removals). Two batches of experiments were conducted: the first batch which took 38 consecutive days achieved a high ammonium removal average (46%) in the first 10 days. Thereafter, because of an increase in the feed volume (concentration of 100 $mgNL^{-1}$), an increase in ammonium concentration was observed. The second batch was conducted for 31 days and compared experiments from coagulation-treated leachate substrates with experiments from raw leachate substrates. Various obstacles were encountered in these experiments, such as controlling pH, dissolved oxygen, conductivity, temperatures and analytical problems, all of which led to a significant, increasing trend of ammonium, nitrate and COD concentrations over the entire set of experiments. More study would be needed before drawing a conclusion in the potential for biological nitrification.

The second system integration (fourth option) investigated the potential for removing ammonium from landfill leachate by combining an adsorption method with a coagulation–flocculation method. The performance of this option was investigated by first treating the leachate using zeolite soil (adsorption method) and then further treating the treated leachate through coagulation–flocculation (using anhydrous ferric chloride and aluminium sulfate). The first treatment through adsorption achieved an average ammonium removal of about 25%, an average COD removal of 11%, 24% colour removal and a 2.0% increase in turbidity concentration. These results are relatively similar to those of individual option two (23% ammonium removal) in Chapter 5. When further treating the adsorption-treated leachate using coagulation–flocculation with anhydrous ferric chloride at pH 7.0, a reduction in ammonia nitrogen concentrations by 14.0% (from 1,521 mg/L to 1,314 mg/L) at a dose of 1,500 mg/L was achieved. This compares well with the previous coagulation–flocculation (option one) results in Chapter 4 (4.4.2.2), where a maximum of 20% ammonia nitrogen removal was obtained at a dose of 2,000 mg/L, while a dose of 1,500 mg/L achieved only 5.0%. The integration of adsorption with anhydrous ferric chloride at pH 7.0 achieved the highest total ammonia nitrogen removal of 36%.

Only 7.0% (from 1,544 mg/L to 1,435 mg/L) of ammonia nitrogen removal was achieved by coagulation–flocculation with alum at pH 6.5, therefore making a total ammonia nitrogen removal of 30% with system integration. In summary, the system integration between adsorption and anhydrous ferric chloride performed better than with alum, achieving the highest ammonia nitrogen removal (36%) at a low coagulant dose of 1,500 mg/L.

The COD results showed a reduction in COD by 39% and 41% from the adsorption-treated leachate using coagulation–flocculation with anhydrous ferric chloride at pH 6.5 and 7.0 respectively, thus achieving a total COD removal of 47% for both pH values with system integration adsorption. Moreover, a better colour treatment (96% removal at a dose of 3,000 mg/L) was obtained by experiments integrating adsorption with anhydrous ferric chloride at pH 6.5, while 89% colour reductions at the same dose of 3,000 mg/L were achieved by experiments that integrated adsorption with anhydrous ferric chloride at pH 7.0. Experiments with integrating adsorption with alum obtained high (93%) colour reductions, at a high dose of 12,000 mg/L, however. The best turbidity treatment (85%) was also achieved by integrating adsorption with anhydrous ferric chloride at pH 6.5 while anhydrous ferric chloride at pH 7.0 produced about 75% reduction.

The system integration of adsorption method with coagulation–flocculation achieved maximum reductions of ammonia nitrogen, COD, colour and turbidity from landfill leachate, of 36%, 47%, 96% and 85% respectively. However, this treatment still produces landfill leachate with high (1,450 mg/L) ammonia nitrogen concentrations which is too high because of the reasons above.

8.3 Limitations of work

Most of the limitations encountered in this study were during the experimental work and these are detailed below.

Optimisation analysis on anhydrous ferric chloride was not conducted during coagulation–flocculation (option one) due to its unavailability at the initial stage of this research. Optimisation is a key component of coagulation–flocculation that could influence the outcome of the results. Moreover, the effect of polyelectrolytes addition was not assessed on anhydrous ferric chloride rather than the hydrated form which could also potential influence the outcome of the results.

Challenges were also encountered in this study during adjustments of leachate sample pH (below 7.0 and above 8.0) with the addition of hydrochloric acid and sodium hydroxide. Rapid foaming occurred which made it difficult to adjust the pH to the desired levels, despite several attempts to mitigate this problem by adding drops of antifoaming agent (amyl alcohol). This could, therefore, have had an influence on the outcome of the results.

Some challenges were due to analytical problems. The leachate sample used was the real-world leachate, not the synthetic type. This leachate contains various pollutants, of which some could interfere with spectrometer analytical analysis, therefore some of the methods struggled with leachate samples. Most of the methods used were developed for the clear sample not for real world leachate samples. Other limitations are that this study examined only one landfill leachate and also other sorbents were not tested.

8.4 Recommendations for future work

This study presented results of the potential of different methods in removing ammonia nitrogen from landfill leachate. However, the ammonia nitrogen removal obtained by biological nitrification method was found to be very low and variable compared with typical

ammonia removal by the conventional wastewater treatment plant or aerated wastewater lagoons. The following suggestions might enhance the ammonia nitrogen removal by the biological nitrification method:

- A batch scale apparatus/reactor that is automated to maintain minimum and maximum dissolved oxygen levels of 0.5 mg/L and 5.0 mg/L respectively should be used. Nitrifying microbes depend on adequate dissolved oxygen to work on ammonia.
- This study did not consider the removal of BOD prior to biological nitrification, which is a very important parameter to consider. The nitrifying microbes cannot compete well with the bacteria that remove BOD (heterotrophic bacteria). Therefore, with high BOD levels in the leachate, the nitrifying microbes are inhibited.
- An automated batch reactor would be able to control and maintain the optimal pH of the biological population thus achieving optimum ammonia nitrogen treatment rates. The nitrifying microbes are very sensitive to pH and decrease significantly with pH values below pH 6.5.
- A method that is better able to retain the nitrifying biomass, such as a fixed film system would be ideal. This would assist with the growth of microorganisms on the retaining medium, and biofilm formation, hence would oxidise ammonia.

The goal of this study was to find leachate pretreatment methods that are effective, simple in operation, low in capital cost, and that result in reduced operational costs.
Further investigations on the adsorption option would be beneficial, that is, identifying soils that are known to have a high clay mineral component and using them as adsorbents. As shown by the results in Chapter 5, the ammonium removal performance of soils depended on the clay content. High clay content results in a high affinity for cations, hence has a high potential for ammonia removal from wastewaters or landfill leachate. Therefore, clay content is very suitable in predicting the ammonium adsorption by soils.

Lastly, the results of ammonia nitrogen removal in the system integration of adsorption and coagulation–flocculation using anhydrous ferric chloride indicate that doses beyond 1,000 mg/L of coagulant caused a decline in ammonia nitrogen removal. It would be very interesting, therefore, to examine the effect of anhydrous ferric chloride doses lower than 1,000 mg/L.

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Appendix A : Typical developed country landfill leachate composition (Johannessen, 1999).

	Average	Range
Acidic phase		
pH	6.1	4.5 – 7.5
BOD_5 (mg/l)	13,000	4,000 – 40,000
COD (mg/l)	22,000	6,000 – 60,000
BOD_5/COD	0.58	
SO_4 (mg/l)	500	70 – 1,750
Ca (mg/l)	1,200	10 – 2,500
Mg (mg/l)	470	50 – 1,150
Fe (mg/l)	780	20 – 2,100
Mn (mg/l)	25	0.3 – 65
Zn (mg/l)	5	0.1 – 120
Methanogenic phase		
pH	8	7.5 – 9
BOD_5 (mg/l)	180	20 – 550
COD (mg/l)	3,000	500 – 4,500
BOD_5/COD	0.06	
SO_4 (mg/l)	80	10 – 420
Ca (mg/l)	60	20 – 600
Mg (mg/l)	180	40 – 350
Fe (mg/l)	15	3 – 280
Mn (mg/l)	0.7	0.03 – 45
Zn (mg/l)	0.6	0.03 – 4
No differences between phases	**Average**	**Range**
Cl (mg/l)	2,100	100 – 5,000
Na (mg/l)	1,350	50 – 4,000
K (mg/l)	1,100	10 – 2,500
Alkalinity (mg $CaCO_3$/l)	6,700	300 – 11,500
NH_4 (mg N/l)	750	30 – 3,000
orgN (mg N/l)	600	10 – 4,250
total N (mg N/l)	1,250	50 – 5,000
NO_3 (mg N/l)	3	0.1– 50
NO_2 (mg N/l)	0.5	0 – 25
total P (mg P/l)	6	0.1 – 30
AOX (µg Cl/l)*	2,000	320 – 3,500
As (µg/l)	160	5 – 1,600
Cd (µg/l)	6	0.5 – 140
Co (µg/l)	55	4 – 950
Ni (µg/l)	200	20 – 2,050
Pb (µg/l)	90	8 – 1,020
Cr (µg/l)	300	30 – 1,600
Cu (µg/l)	80	4 – 1,400
Hg (µg/l)	10	0.2 – 50

*absorbable organic halogen

Appendix B : Landfill Leachate composition from different countries (Renou et al., 2007).

Age	Landfill site	COD	BOD	BOD/COD	pH	SS	TKN	NH_3-N	Reference
Y	Canada	13,800	9660	0.7	5.8	-	212	42	Henry et al. 1987
Y	China, Hong Kong	15,700	4200	0.27	7.7	-	-	2,600	Lau et al. 2001
Y	China, Hong Kong	17,000	7300	0.43	7.0-8.3	>5000	3,200	3,000	Lo et al. 1996
Y		13,000	5000	0.38	6.8-9.1	2000	11,000	11,000	
Y		50,000	22,000	0.44	7.8-9.0	2000	13,000	13,000	
Y	China, Mainland	1900-3180	3700-8890	0.36-0.51	7.4-8.5	-	-	630-1800	Wang et al. 2000
Y	Greece	70,900	26,800	0.38	6.2		3,400	3,100	Tsatsi et al. 2003
Y	Italy	19,900	4000	0.2	8	950	-	3,917	Di Palma et al. 2002
Y	Italy	10,540	2,300	0.22	8.2	-	-	5,210	Lopez et al. 2004
Y	South Korea	24,400	10,800	0.44	7.3	1666	1,760	1,682	Im et al. 2001
Y	Turkey	16,200-20,000	10,800-11,000	0.55-0.67	7.3-7.8	2400	-	1,120-2,500	Timur et al. 1999
Y	Turkey	35,000-50,000	21,000-25,000	0.5-0.6	5.6-7.0	-	2,370	2,020	Ozturk et al. 2001
Y	Turkey	35,000-50,000	21,000-25,000	0.5-0.6	5.6-7.0	2630-3930	-	1,946-2,002	Cecen et al. 2004
MA	German	3180	1436	0.33	-	-	1,134	884	Van dijk et al. 1997
MA	German	4000	1060	0.2	-	-	-	800	Frascari et al. 2004
MA	Taiwan	6500	500	0.08	8	-	-	5,500	Wu et al. 2004
O	Brazil	3460	150	0.04	8.2	-	-	800	Silva et al. 2004
O	Estonia	2170	800	0.37	11.5	-	-	-	Orupold et al. 2000
O	Finland	556	62	0.11	-	-	192	159	Hoilijoki et al. 2000
O	Finland	340-920	84	0.09-0.25	7.1-7.6	-	-	330-560	Silva et al. 2004
O	France	500	7.1	0.01	7.5	130	540	430	Trebouet et al. 1999
O	France	100	3	0.03	7.7	13-1480	5-960	0.2	Tabet et al. 2002
O	South Korea	1409	62	0.04	8.57	404	141	1522	Cho et al. 2003

Y: young; MA: medium age; O: old (values in mg/L except BOD/COD and pH)

Appendix C : Old landfill Leachate composition from Denmark (Kjeldsen & Christophersen, 2000).

	Number of observations	Percentage of wells detected	Average[1]	Standard deviation
pH	131	100	7.0	0.51
Spec. conductivity (mS m^{-1})	118	100	300	250
Calcium (mg l^{-1})	90	100	280	210
Magnesium (mg l^{-1})	79	100	60	77
Sodium (mg l^{-1})	96	100	210	370
Potassium (mg l^{-1})	85	100	140	320
Total iron (mg l^{-1})	80	100	76	380
Ammonia (mg l^{-1})	104	100	110	190
Total phosphorus (mg l^{-1})	70	100	1.5	5.5
Manganese (mg l^{-1}l)	77	100	3.5	8.1
Chloride (mg l^{-1})	117	100	360	750
Bi-carbonate (mg l^{-1})	61	100	4100	16000
Sulphate (mg l^{-1})	88	100	150	220
Methane (mg l^{-1})	17	100	22	60
BOD5 (mg l^{-1})	35	100	44	120
COD (mg l^{-1})	85	100	320	550
BOD5/COD (–)	35	100	0.11	-
TOC (mg l^{-1})	32	100	130	430
NVOC (mg l^{-1})	57	100	82	140
AOX (mg l^{-1})	41	99	1.1	8.5
Benzene (µg l^{-1})	62	55	22	65
Toluene (µg l^{-1})	63	49	38	240
Xylene (µg l^{-1})	63	73	210	2000
Ethylbenzene (µg l^{-1})	10	60	30	46
Naphthalene (µg l^{-1})	27	70	34	140
Chloroform (µg l^{-1})	14	50	0.39	0.38
1,1,1-Trichloroethane (µg l^{-1})	20	60	3.3	15
Trichlorethylene (µg l^{-1})	23	40	5.6	44
Tetrachlorethylene (µg l^{-1})	23	57	3.2	16
Phenols (µg l^{-1})	76	82	23	87
Cresols (µg l^{-1})	37	78	17	98
Xylenoles (µg l^{-1})	37	86	27	160
Lead (µg l^{-1})	58	93	70	460
Zinc (µg l^{-1})	35	89	670	4500
Cadmium (µg l^{-1})	55	27	6.8	11
Chromium (µg l^{-1})	30	90	76	320
Copper (µg l^{-1})	29	97	70	300
Arsenic (µg l^{-1})	20	85	16	32
Nickel (µg l^{-1})	35	83	130	370
Mercury (µg l^{-1})	35	26	5.2	8.3

[1] For the log-normal distributed concentration data, the average ($\bar{x}$) is calculated using the formula: $\bar{x} = e^{\mu} \cdot e^{V\sigma^2}$ where μ and σ are the mean and standard deviation estimated for the log-transformed concentration data (Metcalfe 1994)

Appendix D : Literature values on ammonia removal via coagulation-flocculation.

Reference		Coag-ulant	pH	Dosage (mg/L)	Initial NH4 (mg/L)	% Removal			
						NH_3-N	COD	SS	Colour
Rui, et al., 2012	Effect of pH	Alum	2	2000	≈1700	3	8	28	31
			7	2000	≈1700	14	33	68	78
			12	2000	≈1700	6	18	30	49
		Ferric	2	2000	≈1700	10	22	63	61
			7	2000	≈1700	26	28	92	82
			12	2000	≈1700	18	20	70	55
	Effect of coagulant dosage	Alum	7	0	≈1700	0	0	0	0
			7	9000	≈1700	26	46	89	92
			7	10000	≈1700	24	42	86	87
		Ferric	7	0	≈1700	0	0	0	0
			7	3000	≈1700	26	37	96	84
			7	5000	≈1700	9	2	10	5
Syafalni, et al., 2012	Effect of pH	Alum	4	12000	2040	-	57.1	-	85.7
			4.8	14000	2040	-	68.9	-	89
			5	16000	2040	-	65.6	-	88
		Lateritic Soil	1.5	12000	2040	-	60	-	70
			2	14000	2040	41.2	65	-	80
			2.5	16000	2040	-	50	-	55
	Effect of Coagulant dosage	Alum	4.8	1000	2040	-	68.9	-	88.9
			4.8	10000	2040	47.6	85.4	-	96.4
			4.8	11000	2040	-	84.9	-	96.2
		Ferric	4.8	2000	2040	-	40	-	61.9
			4.8	14000	2040	-	65.7	-	81.8
			4.8	16000	2040	-	62	-	78.6
Adlan, et al., 2011	With DAF	Ferric	4	1500	1975	55	68.9	-	81.3
			5	812.5	1975	43.2	70.5	-	86.6
			6	1500	1975	50.8	73.5	-	93.2
Moham-med, et al., 2015	Optimum pH and dosage	Alum	7	9400	1949	-	84	96	92
		Poly-alum. chloride	7.5	1900	1949	-	57	99	97
	With DAF	Alum		2300	1949	<5	79	-	70
		Ferric		599	1949	41	75	-	93
Vedrenne et al., 2012	Optimum pH and dosage	Ferric	3	300	381	36.1	17.8	-	-
	With photo-Fenton	Ferric	<7	114	381	64	56	-	-

Appendix E :Polyelectrolyte data sheets.

BASF
The Chemical Company

® = registered Trademark of BASF Corporation

Magnafloc® LT-7991

Potable Water Grade Liquid Cationic Coagulant

Chemical Nature

Aqueous polymer solution of epichlorohydrin amine condensates

Application Areas

Used as a primary coagulant for the clarification of potable water and a wide range of industrial effluents.

American Standard ANSI/NSF 60 compliant for coagulation and flocculation up to a maximum concentration of 20 mg/L.

This product is FDA approved. Contact a sales representative for more information.

Benefits

- Reduction or elimination of inorganic primary coagulants.
- Reduction in sludge volume produced in the system.
- Reduction in overall treatment cost.
- Can be used in combination with inorganic coagulants.
- Decrease in pH sensitivity of coagulation/flocculation process.
- Stable to degradation by chlorine.

Typical Properties

Product type:	Solution polymer
Physical form:	Clear viscous colorless-yellow liquid
Solids content:	50%
Molecular weight:	High
Specific gravity:	1.14
Bulk density:	9.51 lb/gal
pH:	5-7
Supplied viscosity:	4,000-7,500 cP

Storage

Under normal, dry storage conditions within the temperature range 5 – 25 °C (41-77 °F) this product will be stable for at least 24 months. Storage outside the above specified temperature range for long periods may adversely affect the product over a long period and should thus be avoided, if possible.

It is recommended that stock solutions at 0.25 - 0.5% are prepared regularly and for maximum effect such solutions should be used within 5 days. Beyond this period some loss in efficiency of the product may occur.

Packaging

227 kg Drum
1,134 kg Tote
~20,000 kg Bulk

Shipping and Handling

As with all cationic polyelectrolyte polymers this product exhibits toxicity towards fish. It is important that precautions are taken where the product may come into direct contact with fresh water courses, streams and rivers.

Corrosion towards most standard materials of construction is very low. Stainless steel, fiberglass, polyethylene, polypropylene and epoxy coated surfaces are recommended. In some cases aluminum surfaces can be adversely affected.

Spilled product is slippery underfoot, very slippery when wet. Product should be protected from frost. Information on the shipping and handling of this product can be found in the relevant MSDS. Disposal of product must comply with all national, state and local laws.

Health and Safety

Detailed information on this product can be found in the relevant Material Safety Data Sheet (MSDS).

Technical Service

BASF sales representatives and field service technicians are available to give advice and assistance in the running of laboratory tests and machine trials to select the correct product and determine the best application conditions.

Note

The data contained in this publication is based on our current knowledge and experience. In view of the many factors that may affect processing and application of our product, this data does not relieve processors from carrying out their own investigations and tests; neither does this data imply any guarantee of certain properties, nor the suitability of the product for a specific purpose. Any descriptions, drawings, photographs, data, proportions, weights etc. given herein may change without prior information and do not constitute the agreed contractual quality of the product. It is the responsibility of the recipient of our products to ensure that any proprietary rights and existing laws and legislation are observed.

February 2013

BASF Corporation
100 Park Avenue
Florham Park, NJ 07932-0685

Water Solutions

Responsible Care®
Good Chemistry at Work

Safety Data Sheet

May not comply with national legislation; shall be used only as a source of information.

Ciba

1. Identification of the Substance/Preparation and of the Company/Undertaking

Designation/Trade Name: MAGNASOL 589

Use: Coagulant.

Company:
Ciba Spezialitätenchemie AG
Klybeckstrasse 141
CH-4002 BASEL
Schweiz
Tel +41 61 636 1111
Fax +41 61 636 1212

Emergency contact: +41 61 632 0779

2. Composition/Information on Ingredients

Chemical nature:

Aqueous solution of inorganic salts and cationic polymer

Hazardous ingredients		Classification*	Content (%)
CAS-No.: 26062-79-3	2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-, chloride, homopolymer	R 52/53	>= 4 - <= 40
CAS-No.: 1327-41-9 EC-No.: 215-477-2	Aluminum chloride, basic	Xi R 36/38	>= 10 - <= 75

*) The wording of the hazard symbols and R-phrases is specified in chapter 16 if dangerous ingredients are mentioned.

3. Hazards Identification

Classification required according to EU

Irritant.

R phrase(s):

R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

R36/38 Irritating to eyes and skin.

Hazards:

May cause irritation to the gastrointestinal tract if swallowed.
Repeated skin exposure may cause contact dermatitis
Spilled product is slippery underfoot.
May cause irritation to the respiratory system, if mists or sprays maybe inhaled.

4. First-aid Measures

If inhaled:
If conscious place in a safe sitting or recovery position. Keep the casualty at rest. Move to fresh air. Seek medical attention if you feel unwell or if exposure prolonged.

On skin contact:
Remove contaminated clothing. Wash affected skin with plenty of water, shower if necessary. If skin irritation or dermatitis commences or persists seek medical attention.

On contact with eyes:
Rinse immediately with plenty of water for at least 10 minutes taking care to wash under the eyelids. If irritation persists, seek medical attention.

On ingestion:
Do not induce vomiting. Never give anything by mouth to an unconscious person. Check breathing and pulse. Place victim in the recovery position, cover and keep warm. Loosen tight clothing such as a collar, tie, belt or waistband. Seek medical attention. Rinse mouth and then drink plenty of water.

5. Fire-fighting Measures

Suitable extinguishing media:
dry powder, carbon dioxide, water spray, foam

Unsuitable extinguishing media for safety reasons:
No restrictions.

Combustion products:
Carbon oxides., Sulphur oxides, Hydrogen chloride, Nitrogen oxides

Exposure hazards:
Do not release chemically contaminated water into drains, soil or surface water. Sufficient measures must be taken to retain the water used for extinguishing. Dispose of contaminated water and soil according to local regulations.

Special protective equipment:
Chemical protection suit, suitable gloves, boots and self contained breathing apparatus.

6. Accidental Release Measures

Personal precautions:
Wear suitable personal protective clothing and equipment. Breathing apparatus is only required in a fire situation.

Environmental precautions:
Prevent entry into sewege systems, ground and surface waters.

Methods for cleaning-up or taking-up:
Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust).
Scoop into marked containers for disposal as chemical waste.
Large spillages should be neutralised with a suitable alkali, such as sodium carbonate
Contain washwater and dispose of in accordance with local regulations.

7. Handling and Storage

Handling
Safety showers and eyewash facilities should be provided in areas where accidental exposure is foreseeable.
High risk of slipping due to leakage/spillage of product.
Keep away from steel, copper, zinc and silver

Storage requirements:
Safety showers and eyewash facilities should be provided in areas where accidental exposure is foreseeable.
Do not store above 40°C.
Keep only in the original container.
Protect from frost.

8. Exposure Controls and Personal Protection

Technical measures/precautions:
Ensure adequate ventilation, especially in confined areas.

Respiratory protection:
Respiratory protection in case of vapour/aerosol release.

Hand protection:
Chemical resistant protective gloves (EN 374)

Eye protection:
Tightly fitting safety goggles (chemical goggles).

Skin and body protection:
Lightweight protective clothing.

9. Physical and Chemical Properties

Form:	liquid
Colour:	amber
Odour:	solvent-like
pH value:	approx. 2
Melting point:	Not applicable
Boiling point:	approx. 100 °C
Flash point:	> 100 °C
Self-ignition temperature:	Not tested
Explosion hazard:	Not applicable
Fire promoting properties:	Not tested
Vapour pressure:	approx. 12,3 kPa (50 °C)
Density:	approx. 1,2 g/cm3
Relative vapour density (Air):	Not tested
Solubility in water:	miscible
Solubility:	Not tested
Partitioning coefficient n-octanol/water (log Pow):	Not applicable
Viscosity, dynamic:	Not tested
Evaporation rate:	Not tested

10. Stability and Reactivity

Conditions to avoid:
Avoid temperatures above 40°C.

Materials to avoid:
acids, oxidizing agent, With sodium hypochlorite solution, an explosive reaction occurs with the formation of chlorine gas., This product will react with metals to liberate highly flammable H2 gas.

Hazardous decomposition products:
No decomposition expected under normal storage conditions.

11. Toxicological Information

Acute oral toxicity:
rat/LD50: > 2.000 mg/kg
By analogy with a product of similar composition

Acute dermal toxicity:
Not tested

Acute inhalation toxicity:
Not tested

Skin irritation/corrosion:
Irritant. (Conventional method)

Eye irritation/corrosion:
Irritant. (Conventional method)

Skin Sensitization:
Not tested

12. Ecological Information

Toxicity to fish:
96 h/LC50: > 10 mg/l
For the polymer component of this product

Toxicity to aquatic invertebrates:
48 h/EC50: > 10 mg/l
For the polymer component of this product

Toxicity to aquatic plants:

Not tested

Toxicity to microorganisms:

Not tested

Assessment of aquatic toxicity:
Polyaluminium chloride
The unneutralised product is expected to be toxic to fish.

Biodegradation:

Not tested

13. Disposal Considerations

Waste from residue/unused products:
Observe all local regulations.

Contaminated packaging:
Contaminated packaging should be emptied as far as possible and disposed of in the same manner as the substance/product.
Clean packaging material should be subjected to waste management schemes (recovery recycling, reuse) according to local legislation.

14. Transport Information

Land transport (ADR):

Not classified as a dangerous good under transport regulations.

Land transport (RID):

Not classified as a dangerous good under transport regulations.

Sea transport (IMDG):

Not classified as a dangerous good under transport regulations.

Air transport (ICAO/IATA):

Not classified as a dangerous good under transport regulations.

15. Regulatory Information

Regulations of the European Union (Labelling) / National legislation/regulations

Classification required according to EU

Hazard symbol(s):

Xi	Irritant.

R phrase(s):

R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R36/38	Irritating to eyes and skin.

S phrase(s):

S28.1	After contact with skin, wash immediately with plenty of water and soap.
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S61	Avoid release to the environment. Refer to special instructions/safety data sheets.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

16. Other Information

Use:

Restricted use:	THIS MATERIAL IS NOT INTENDED FOR USE IN PRODUCTS FOR WHICH PROLONGED CONTACT WITH MUCOUS MEMBRANES, BODY FLUIDS OR ABRADED SKIN, OR IMPLANTATION WITHIN THE HUMAN BODY, IS SPECIFICALLY INTENDED, UNLESS THE FINISHED PRODUCT HAS BEEN TESTED IN ACCORDANCE WITH NATIONALLY AND INTERNATIONALLY APPLICABLE SAFETY TESTING REQUIREMENTS. BECAUSE OF THE WIDE RANGE OF SUCH POTENTIAL USES, CIBA IS NOT ABLE TO RECOMMEND THIS MATERIAL AS SAFE AND EFFECTIVE FOR SUCH USES AND ASSUMES NO LIABILITY FOR SUCH USES.

R phrases and hazard symbols:

R52/53	**Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.**

R36/38	Irritating to eyes and skin.
Xi	Irritant.

Vertical lines in the left hand margin indicate an amendment from the previous version.

This product should be stored, handled and used in accordance with good industrial hygiene practices and in conformity with any legal regulation. The information contained herein is based on the present state of our knowledge and is intended to describe our products from the point of view of safety requirements. It should not therefore be construed as guaranteeing specific properties.

Appendix F : First batch experiments ammonia nitrogen summary results with anhydrous ferric chloride.

Sample No.	Sample	Weight/Volume (g or ml)	Coagulant	pH	Dosage (mg/L)	Titrant (mL)	Ave. titrant (mL)	NH_3-N (mg/L)	NH_3-N ave. (mg/L)	c.f (mg/L)	NH_3-N removal (%)	Comment/Observations
A	Blank	50 ml	-	-	-	0.04	0.05	-	-	-	-	M03 programm used for titration
B	Blank	50 ml	-	-	-	0.06						
C	QC	10ml QC std-50ml	-	-	-	3.763	-	1040	-	1000	-	
D	QC	10ml QC std-50ml	-	-	-	3.562		985	-	1000	-	
#1a	Raw Leachate	20 ml-50ml	-	-	-	15.130	-	2114	2103.85	-	-	No foaming
#1b	Raw Leachate	20 ml-50ml	-	-	-	15.000	-	2094				
#1a	Coag. Sample	20 ml-50ml	Anhydrous ferric chloride ($FeCl_3$)	7	1000	13.047	-	1822	1841.01	-	12.5	No foaming, colour not reduced, grey flocs and about 20% flocs formed
#1b	Coag. Sample	20 ml-50ml		7	1000	13.33	-	1860				
#2a	Coag. Sample	20 ml-50ml		7	1500	14.505	-	2000	2018.06	-	10.8	No foaming, colour not reduced, grey flocs and about 25% flocs formed
#2b	Coag. Sample	20 ml-50ml		7	1500	14.482	-	2036				
#3a	Coag. Sample	20 ml-50ml		7	1800	12.772	-	1783	1759.42	-	16.4	No foaming, colour not reduced, grey flocs and about 25% flocs formed
#3b	Coag. Sample	20 ml-50ml		7	1800	12.43	-	1735				
#4a	Coag. Sample	20 ml-50ml		7	2000	10.197	-	1419	1435.16	-	36.5	No foaming, colour slightly reduced, grey flocs and about 30% flocs formed
#4b	Coag. Sample	20 ml-50ml		7	2000	10.425	-	1451				
#5a	Coag. Sample	20 ml-50ml		7	2500	11.058	-	1542	1539.09	-	26.8	No foaming, colour slightly reduced, grey flocs and about 30% flocs formed
#5b	Coag. Sample	20 ml-50ml		7	2500	11.008	-	1536				
#6a	Coag. Sample	20 ml-50ml		7	3000	13.992	-	1951	1959.51	-	13.4	Slightly foaming, colour reduced, grey flocs and about 35% flocs formed
#6b	Coag. Sample	20 ml-50ml		7	3000	14.117	-	1968				
#7a	Coag. Sample	20 ml-50ml		7	3500	14.412	-	2009	2014.35	-	10.98	Slightly foam, colour reduced, grey flocs and about 40% flocs formed
#7b	Coag. Sample	20 ml-50ml		7	3500	14.48	-	2019				

Appendix F: First batch experiments COD summary results with anhydrous ferric chloride.

Sample No.	**Sample**	**Dosage** (mg/L)	**Dilution**	**Reading** (mg/L)	**Results** (mg/L)	**Ẍ** (mg/L)	**c.f.** (mg/L)	**COD removal** (%)	**Comment**
A	Blank		-	0	0			-	-
B	QC		-	605	608		600	-	within range
C	QC		-	593	607		600	-	
1	Raw Leachate		x5(20-100)	833	4165	4105	-	-	within range
	Raw Leachate		x5(20-100)	831	4155				
	Raw Leachate		x10(5-50)	413	4130				
	Raw Leachate		x10(5-50)	397	3970				
2	Anhydrous ferric chloride ($FeCl_3$)	1000	x5(20-100)	786	3930	3946	-	3.9	within range
		1000	x5(20-100)	783	3915				
		1000	x10(5-50)	397	3970				
		1000	x10(5-50)	397	3970				
3		1500	x5(20-100)	677	3385	3555	-	28.3	within range
		1500	x5(20-100)	691	3455				
		1500	x10(5-50)	376	3760				
		1500	x10(5-50)	362	3620				
4		1800	x5(20-100)	710	3550	3638	-	11.4	within range
		1800	x5(20-100)	700	3500				
		1800	x10(5-50)	375	3750				
		1800	x10(5-50)	375	3750				
		2000	x5(20-100)	513	2565	2444	-	50.7	Within range and good results
		2000	x5(20-100)	484	2420				
		2000	x10(5-50)	239	2390				
		2000	x10(5-50)	240	2400				
5		2500	x5(20-100)	664	3320	3380	-	17.7	within range
		2500	x5(20-100)	642	3210				
		2500	x10(5-50)	351	3510				
		2500	x10(5-50)	348	3480				
6		3000	x5(20-100)	644	3220	3300	-	33.5	Within range and good results
		3000	x5(20-100)	646	3230				
		3000	x10(5-50)	345	3450				
		3000	x10(5-50)	330	3300				
7		3500	x5(20-100)	-	3150	3090	-	37.7	Within range and good results
		3500	x5(20-100)	-	3120				
		3500	x10(5-50)	-	3040				
		3500	x10(5-50)	-	3050				

Appendix F-1: First batch experiments ammonia nitrogen results with alum.

Sample No.	Sample	Weight/Volume (g or mL)	Coagulant	pH	Dosage (mg/L)	Titrant (mL)	Ave. titrant (mL)	NH_3-N (mg/L)	NH_3-N ave. (mg/L)	c.f (mg/L)	NH_3-N removal (%)	Comment/Observations
A	Blank	50 ml	-	-	-	0.06	0.065	-	-	-	-	M03 programme used for titration
B	Blank	50 ml	-	-	-	0.07		-	-	-		
C	QC	10ml QC std-50ml	-	-	-	3.50	-	966		1000	-	
D	QC	10ml QC std-50ml	-	-	-	3.58	-	989		1000	-	
#1a	Coag. Sample	20 ml-50ml	Alum	7	1000	14.04		1961	1967	-	6.5	No foaming, colour not reduced, light brown flocs and about 2% flocs formed
#1b	Coag. Sample	20 ml-50ml		7	1000	14.13		1972		-		
#2a	Coag. Sample	20 ml-50ml		7	1500	13.87		1937	1942	-	7.7	No foaming, colour not reduced, light brown flocs and about 4% flocs formed
#2b	Coag. Sample	20 ml-50ml		7	1500	13.95		1948		-		
#3a	Coag. Sample	20 ml-50ml		7	1800	13.99		1953	1960	-	6.9	No foaming, colour not reduced, light brown flocs and about 4% flocs formed
#3b	Coag. Sample	20 ml-50ml		7	1800	14.078		1966		-		
#4a	Coag. Sample	20 ml-50ml		7	2000	14.20		1983	1969	-	6.4	No foaming, colour not reduced, light brown flocs and about 4% flocs formed
#4b	Coag. Sample	20 ml-50ml		7	2000	14.00		1954		-		
#5a	Coag. Sample	20 ml-50ml		7	2500	13.67		1908	1911	-	9.2	No foaming, colour not reduced, light brown flocs and about 10% flocs formed
#5b	Coag. Sample	20 ml-50ml		7	2500	13.697		1913		-		
#6a	Coag. Sample	20 ml-50ml		7	3000	14.03		1957	1952	-	7.2	No foaming, colour slightly reduced, light brown flocs and about 10% flocs formed
#6b	Coag. Sample	20 ml-50ml		7	3000	13.94		1947		-		
#7a	Coag. Sample	20 ml-50ml		7	4000	13.66		1908	1917	-	8.9	No foaming, colour slightly reduced, light brown flocs and about 17% flocs formed

#7b	Coag. Sample	20 ml-50ml		7	4000	13.793	-	1925		-		
#8a	Coag. Sample	20 ml-50ml		7	5000	13.978	-	1952	1939	-	7.8	No foaming, colour slightly reduced, light brown flocs and about 17% flocs formed
#8b	Coag. Sample	20 ml-50ml		7	5000	13.787	-	1926				
#9a	Coag. Sample	20 ml-50ml		7	6000	12.87	-	1796	17999	-	14.5	slightly foaming, colour reduced, light brown flocs and about 23% flocs formed
#9b	Coag. Sample	20 ml-50ml		7	6000	12.908	-	1802				
#10a	Coag. Sample	20 ml-50ml		7	7000	13.665	-	1908	1934	-	8.1	slightly foaming, colour reduced, light brown flocs and about 25% flocs formed
#10b	Coag. Sample	20 ml-50ml		7	7000	14.03	-	1958				
#11a	Coag. Sample	20 ml-50ml		7	8000	14.355	-	2005	2003	-	4.8	foaming, colour reduced, light brown flocs and about 25% flocs formed
#11b	Coag. Sample	20 ml-50ml	Alum	7	8000	14.318	-	2000				
#12a	Coag. Sample	20 ml-50ml		7	9000	13.902	-	1940	1935	-	8.03	foaming, colour reduced, light brown flocs and about 30% flocs formed
#12b	Coag. Sample	20 ml-50ml		7	9000	13.815	-	1929				
#13a	Coag. Sample	20 ml-50ml		7	10000	13.605	-	1900	1920	-	8.7	foaming, colour reduced, light brown flocs and about 33% flocs formed
#13b	Coag. Sample	20 ml-50ml		7	10000	13.9	-	1940				
#14a	Coag. Sample	20 ml-50ml		7	12000	13.388	-	1870	1877	-	10.8	slightly foaming, colour reduced, light brown flocs and about 46% flocs formed
#14b	Coag. Sample	20 ml-50ml		7	12000	13.495	-	1885				
#15a	Coag. Sample	20 ml-50ml		7	14000	13.45	-	1877	1892	-	10.1	slightly foaming, colour reduced, light brown flocs and about 50% flocs formed
#15b	Coag. Sample	20 ml-50ml		7	14000	13.66	-	1908				

C.f *– comparison values*

Appendix F-1: First batch experiments COD nitrogen results with alum.

Sample No.	Sample	Dosage (mg/L)	Dilution	Reading (mg/L)	Results (mg/L)	Ẍ (mg/L)	c.f. (mg/L)	COD removal (%)	Comment
A	Blank	-	-	0	0	-	-	-	-
B	QC	-	-	576	576	-	600	-	within range
C	QC	-	-	585	585	-	600	-	within range
1	Alum	1000	x5(20-100)	773	3865	3935		4.1	within range
		1000	x5(20-100)	783	3915				
		1000	x10(5-50)	403	4030				Within range
		1000	x10(5-50)	393	3930				
2		1500	x5(20-100)	783	3915	3901		5.0	within range
		1500	x5(20-100)	788	3940				
		1500	x10(5-50)	394	3940				Within range
		1500	x10(5-50)	381	3810				
3		1800	x5(20-100)	680	3400	3488		15.0	within range
		1800	x5(20-100)	678	3390				
		1800	x10(5-50)	367	3670				Within range
		1800	x10(5-50)	349	3490				
4		2000	x5(20-100)	768	3840	3804		7.3	within range
		2000	x5(20-100)	771	3855				
		2000	x10(5-50)	377	3770				Within range
		2000	x10(5-50)	375	3750				
5		2500	x5(20-100)	755	3775	3781		7.9	within range
		2500	x5(20-100)	740	3700				
		2500	x10(5-50)	380	3800				Within range
		2500	x10(5-50)	385	3850				
6		3000	x5(20-100)	717	3585	3736		9.0	within range
		3000	x5(20-100)	720	3600				
		3000	x10(5-50)	390	3900				Within range
		3000	x10(5-50)	386	3860				
7		4000	x5(20-100)	720	3600	3603		12.2	within range
		4000	x5(20-100)	720	3600				
		4000	x10(5-50)	361	3610				Within range
		4000	x10(5-50)	360	3600				
8		5000	x5(20-100)	695	3475	3528		14.0	within range
		5000	x5(20-100)	700	3500				
		5000	x10(5-50)	361	3610				Within range

Sample No.	Sample	Dosage (mg/L)	Dilution	Reading (mg/L)	Results (mg/L)	Ẍ (mg/L)	c.f. (mg/L)	COD removal (%)	Comment
9	Alum	6000	x5(20-100)	639	3195	3235		21.2	Within range
		6000	x5(20-100)	642	3210				
		6000	x10(5-50)	330	3300				
10		7000	x5(20-100)	682	3410	3420		16.7	within range
		7000	x5(20-100)	686	3430				
		7000	x10(5-50)	-	-				
11		8000	x5(20-100)	643	3215	3373		17.8	within range
		8000	x5(20-100)	-	-				
		8000	x10(5-50)	353	3530				
12		9000	x5(20-100)	626	3130	3217		21.6	within range
		9000	x5(20-100)	630	3150				
		9000	x10(5-50)	337	3370				
13		10000	x5(20-100)	631	3155	3105		24.4	within range
		10000	x5(20-100)	626	3130				
		10000	x10(5-50)	303	3030				
14		12000	x5(20-100)	619	3095	2967		27.7	within range
		12000	x5(20-100)	569	2845				
		12000	x10(5-50)	296	2960				
15		14000	x5(20-100)	530	2650	2625		36.1	within range
		14000	x5(20-100)	535	2675				
		14000	x10(5-50)	255	2550				

Appendix G : Second batch experiments ammonia nitrogen results with anhydrous ferric chloride.

Sample No.	Sample	Weight/Volume (g or mL)	Coagulant	pH	Dosage (mg/L)	Titrant (mL)	Ave. titrant (mL)	NH_3-N (mg/L)	NH_3-N ave. (mg/L)	c.f (mg/L)	NH_3-N removal (%)	Comment
A	Blank	50 ml		-	-	0.07	0.075					M03 programme used for titration
B	Blank	50 ml		-	-	0.08						
C	QC	10ml QC std- 50ml		-	-	3.64		999		1000		
D	QC	10ml QC std- 50ml		-	-	3.68		1010		1000		
#1a	Raw leachate	20 ml-50ml	-	7	-	15.100		2105	2119			No foaming. No colour change, no flocs
#1b	Raw leachate	20 ml-50ml		7	-	15.298		2132				
#2a	Coag. Sample	20 ml-50ml	Anhydrous ferric chloride ($FeCl_3$)	7	1,000	14.465		2016	2018		4.8	No foaming. No colour change, 50/300 flocs, grey flocs
#2b	Coag. Sample	20 ml-50ml		7	1,000	14.488		2019				
#3a	Coag. Sample	20 ml-50ml		7	1,500	14.25		1986	2013		5.0	No foaming. No colour change, 50/300 flocs, grey flocs
#3b	Coag. Sample	20 ml-50ml		7	1,500	14.638		2040				
#4a	Coag. Sample	20 ml-50ml		7	1,800	13.78		1920	1911		9.8	Slight foaming, slight colour change, 70/300 flocs, grey flocs
#4b	Coag. Sample	20 ml-50ml		7	1,800	13.657		1902				
#5a	Coag. Sample	20 ml-50ml		7	2,000	12.167		1694	1686		20.4	Slight foaming, no colour change, 100/300 flocs, grey flocs
#5b	Coag. Sample	20 ml-50ml		7	2,000	12.056		1678				
#6a	Coag. Sample	20 ml-50ml		7	2,500	14.012		1953	1959		7.5	Slight foaming, slight colour change, 80/300 flocs, grey flocs
#6b	Coag. Sample	20 ml-50ml		7	2,500	14.105		1965				
#7a	Coag. Sample	20 ml-50ml		7	3,000	13.833		1928	1953		7.8	Foaming, slight colour change, 100/300 flocs, grey flocs
#7b	Coag. Sample	20 ml-50ml		7	3,000	14.205		1979				
#8a	Coag. Sample	20 ml-50ml		7	3,500	13.205		1840	1851		12.6	Foaming, colour reduced, 100/300 flocs, grey flocs
#8b	Coag. Sample	20 ml-50ml		7	3,500	13.375		1863				
#9a	Coag. Sample	20 ml-50ml		7	4,000	13.87		1933	1927		9.1	Foaming, colour reduced, 100/300 flocs, grey flocs
#9b	Coag. Sample	20 ml-50ml		7	4,000	13.79		1921				
#10a	Coag. Sample	20 ml-50ml		7	4,500	14.055		1959	1953		7.8	Foaming, colour reduced, 110/300 flocs, grey flocs
#10b	Coag. Sample	20 ml-50ml		7	4,500	13.98		1948				
#11a	Coag. Sample	20 ml-50ml		7	5,000	13.232		1844	1848		12.8	Foaming, colour reduced, 120/300 flocs, grey flocs
#11b	Coag. Sample	20 ml-50ml		7	5,000	13.3		1852				

Appendix G-1: Second batch experiments COD results with anhydrous ferric chloride.

Sample	**Dosage** (mg/L)	**Dilution**	**Reading** (mg/L)	**Results** (mg/L)	**Ẍ** (mg/L)	**c.f.** (mg/L)	**COD removal** (%)	**Comment**
Blank	-	-	0	0	-	-	-	-
QC	-	-	569	569	569	600	-	within range
QC	-	-	607	607	607	600	-	within range
Anhydrous ferric chloride ($FeCl_3$)	1,000	x5(20-100)	661	3305	3408	-	17.0	within range
	1,000	x5(20-100)	692	3460				
	1,000	x10(5-50)	346	3460				within range
	1,500	x5(20-100)	677	3385	3310	-	19.4	
	1,500	x5(20-100)	679	3395				within range
	1,500	x10(5-50)	315	3150				
	1,800	x5(20-100)	651	3255	3260	-	20.6	within range
	1,800	x5(20-100)	655	3275				
	1,800	x10(5-50)	325	3250				within range
	2,000	x5(20-100)	600	3000	2937	-	28.5	
	2,000	x5(20-100)	602	3010				within range
	2,000	x10(5-50)	280	2800				
	2,500	x5(20-100)	604	3020	2975	-	27.5	within range
	2,500	x5(20-100)	615	3075				
	2,500	x10(5-50)	283	2830				Within range
	3,000	x5(20-100)	602	3010	2977	-	27.5	
	3,000	x5(20-100)	610	3050				within range
	3,000	x10(5-50)	287	2870				
	3,500	x5(20-100)	559	2795	2855	-	30.5	Within range
	3,500	x5(20-100)	583	2915				
	4,000	x5(20-100)	533	2665	2803	-	31.7	
	4,000	x5(20-100)	588	2940				Within range
	4,500	x5(20-100)	603	3015	2965	-	27.8	within range
	4,500	x5(20-100)	583	2915				
	5,000	x5(20-100)	551	2755	2780	-	32.3	within range
	5,000	x5(20-100)	561	2805				

Appendix H : Experiments with hexahydrate ferric chloride showing ammonia test results.

Sample No.	Sample	Weight/Volume (g or mL)	Coagulant	pH	Dosage (mg/L)	Titrant (mL)	Ave. Titrant (mL)	NH_3-N (mg/L)	NH_3-N ave. (mg/L)	c.f (mg/L)	NH_3-N removal (%)	Comment/Observations
A	Blank	50 ml	-	-	-	0.08	0.075	-	-	-	-	M03 program used for titration
B	Blank	50 ml	-	-	-	0.07		-		-	-	
C	QC	10ml QC std- 50ml	-	-	-	3.625	3.625	995	995	1000		
D	QC	10ml QC std- 50ml	-	-	-	3.63	3.63	996	996	1000		
#1a	Coag. Sample	20 ml-50ml	Hexahydrate ferric chloride	7	1,000	14.7	14.7	2049	2041	-	3.9	No foaming, colour not reduced, grey flocs and about 2% flocs formed
#1b	Coag. Sample	20 ml-50ml		7	1,000	14.59	14.59	2033				
#2a	Coag. Sample	20 ml-50ml		7	1,500	14.8	14.8	2063	2058	-	3.1	No foaming, colour not reduced, grey flocs and about 10% flocs formed
#2b	Coag. Sample	20 ml-50ml		7	1,500	14.74	14.74	2054				
#3a	Coag. Sample	20 ml-50ml		7	1,800	14.8	14.8	2063	2058		3.1	No foaming, colour not reduced, grey flocs and about 14% flocs formed
#3b	Coag. Sample	20 ml-50ml		7	1,800	14.74	14.74	2054		-		
#4a	Coag. Sample	20 ml-50ml		7	2,000	14.55	14.55	2028	2012	-	5.3	No foaming, colour not reduced, grey flocs and about 10% flocs formed
#4b	Coag. Sample	20 ml-50ml		7	2,000	14.33	14.33	1997				
#5a	Coag. Sample	20 ml-50ml		7	2,500	14.65	14.65	2042	2021	-	4.8	No foaming, colour reduced, grey flocs and about 18% flocs formed
#5b	Coag. Sample	20 ml-50ml		7	2,500	14.36	14.36	2001				
#6a	Coag. Sample	20 ml-50ml		7	3,000	13.7	13.7	1913	1928	-	9.2	slightly foaming, colour reduced, grey flocs and about 34% flocs formed
#6b	Coag. Sample	20 ml-50ml		7	3,000	13.905	13.905	1942				
#7a	Coag. Sample	20 ml-50ml		7	3,300	13.893	13.893	1940	1939	-	9.17	foaming, colour reduced, grey flocs and about 38% flocs formed
#7b	Coag. Sample	20 ml-50ml		7	3,300	13.745	13.745	1920				
#8a	Coag. Sample	20 ml-50ml		7	3,300	14.015	14.015	1957		-		
#8b	Coag. Sample	20 ml-50ml		7	3,300	13.3	13.3	1857				
#9a	Coag. Sample	20 ml-50ml		7	4,166	13.87	13.87	1937	1897	-	8.7	Foaming, colour reduced, grey flocs and 30% flocs formed
#9b	Coag. Sample	20 ml-50ml		7	4,166	13.9	13.9	1941				
#10a	Coag. Sample	20 ml-50ml		7	4,166	14.05	14.05	1962		-		
#10b	Coag. Sample	20 ml-50ml		7	4,166	14.2	14.2	1983				
#11a	Coag. Sample	20 ml-50ml		7	5,000	14.463	14.463	2020	2010	-	5.4	foaming, colour reduced, grey flocs and about 35% flocs formed
#11b	Coag. Sample	20 ml-50ml		7	5,000	14.312	14.312	1999				

Appendix H: Experiments with hexahydrate ferric chloride showing COD test results from raw data.

Sample No.	**Sample**	**Coagulant Dose** (g/L)	**Dilution**	**Reading** (mg/L)	**Results** (mg/L)	**c.f** (mg/L)	**Ẍ** (mg/L)	**COD Removal** (%)	**Comment**
A	Blank	-	-	0	0		-	-	within range
B	QC	-	-	588	588	600	-	-	
C	QC	-	-	612	612	600	-	-	
1	Coag. Sample	1	x5(20-100)	728	3640	-	3720	12.2	Decrease
	Coag. Sample	1	x10(5-50)	380	3800	-			
2	Coag. Sample	1.5	x5(20-100)	714	3570	-	3350	20.9	Decrease
	Coag. Sample	1.5	x10(5-50)	313	3130	-			
3	Coag. Sample	1.8	x5(20-100)	716	3580	-	3690	12.9	Decrease
	Coag. Sample	1.8	x10(5-50)	380	3800	-			
4	Coag. Sample	2	x5(20-100)	779	3895	-	3922.5	7.4	Decrease
	Coag. Sample	2	x10(5-50)	395	3950	-			
5	Coag. Sample	2.5	x5(20-100)	835	4175	-	4062.5	4.1	Decrease
	Coag. Sample	2.5	x10(5-50)	395	3950	-			
6	Coag. Sample	3	x5(20-100)	669	3345	-	3522.5	16.9	Decrease
	Coag. Sample	3	x10(5-50)	370	3700	-			
7	Coag. Sample	3.3	x5(20-100)	695	3475	-	3437.5	18.9	Decrease
	Coag. Sample	3.3	x10(5-50)	340	3400	-			
8	Coag. Sample	4.2	x5(20-100)	630	3150	-	3175	25.1	Decrease
	Coag. Sample	4.2	x10(5-50)	320	3200	-			
9	Coag. Sample	5	x5(20-100)	650	3250	-	3125	26.2	Decrease
	Coag. Sample	5	x10(5-50)	300	3000	-			

Appendix I : Summary results of experiments with hexahydrate ferric chloride with polyelectrolytes.

Coagulant	Polyelectrolyte	Coagulant dosage (g/L)	pH	Polymer dose (mL/L)	NH_3-N removal (%)	COD removal (%)	Turbidity removal/conc. (%)	NTU
Hexahydrate Ferric chloride: $FeCl_3.6H_2O$ (M = 270.30g/mol)	Control	3	7	0	9.2	16.9	11.5	58.4
	Magnesol 589	3	7	1	4.9	21.3	(128)	133
		3	7	2	6.4	27.7	(13.2)	66.1
		3	7	3	5.8	31.9	34.6	38.2
		3	7	4	6.9	37.5	69.2	18
		3	7	5	5.5	45.1	87.3	7.4
		3	7	10	5.3	33.6	71.2	16.8
		3	7	20	5.3	(9.0)	90.4	5.59
		3	7	30	6.1	(24.0)	93.8	3.63
	Crystalfloc	3	7	5	7.0	6	(150)	146
		3	7	10	4.1	5.36	(260)	210
		3	7	15	0.9	14.92	(164)	154
		3	7	20	6.0	0.28	(489)	344
		3	7	25	3.8	(5.2)	(81)	106
	Magnafloc LT- 7991	3	7	1	5.7	25.42	(450)	321
		3	7	3	7.0	13.62	27.4	42.4
		3	7	5	5.5	1.97	56.5	25.4
		3	7	10	6.8	(32.3)	(139)	139
		3	7	15	6.4	(42.8)	67.5	19
		3	7	20	8.1	(57.2)	(67.1)	97.6

Note: values in brackets () are negative values

Appendix J : Hydrometer sedimentation process raw data sheets and zeolite data sheets

Sample Name: Type A
Depth:
Date:
Tested By: Doctor

Pre-Hydrometer WC

air dried mass + bowl	51
M dry + bowl	49.79
M bowl	49.71
WC	37.90
	#DIV/0!

Mass of Sample used in Hydrometer

As Tested Mass	65.64	176.52
Dry Mass	#DIV/0!	149.39

Gs	2.69
Assumed/Measured	Assumed

Hydrometer Analysis

Hydrometer ID	350469
j1	164.21
j2	2.656
Cm	0.25
R0 at start	

Note: not necessary to remeasure unless Temp changes by

Summary

particle size	cum % passing
2.36	#DIV/0!
1.18	#DIV/0!
0.600	#DIV/0!
0.425	#DIV/0!
0.300	#DIV/0!
0.212	#DIV/0!
0.150	#DIV/0!
0.075	#DIV/0!
0.063	#DIV/0!
#DIV/0!	**#DIV/0!**
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!

t (min)	Temp	R'h	R0	Rh	HR	nu	D
2	22	21	21	0.25	163.5460	1.7604	#DIV/0!
5	22	18.5		0.25	163.5460	1.7604	#DIV/0!
15	22	16		0.25	163.5460	1.7604	#DIV/0!
30	22	14.8		0.25	163.5460	1.7604	#DIV/0!
60	22	13.8		0.25	163.5460	1.7604	#DIV/0!
240	22	12		0.25	163.5460	1.7604	#DIV/0!
1440	21.5	10		0.25	163.5460	1.7604	#DIV/0!

Sieve size	mass	% retained	cum. % passing
2.36	0	#DIV/0!	#DIV/0!
1.18	0	#DIV/0!	#DIV/0!
0.6	0.04	#DIV/0!	#DIV/0!
0.425	0.05	#DIV/0!	#DIV/0!
0.3	0.09	#DIV/0!	#DIV/0!
0.212	0.19	#DIV/0!	#DIV/0!
0.15	3.78	#DIV/0!	#DIV/0!
0.075	14.8	#DIV/0!	#DIV/0!
0.063	3.43	#DIV/0!	#DIV/0!
total	0		
fines	#DIV/0!	#DIV/0!	

= 0.11

pan = 0.35

Sample Name:	Type B
Depth:	
Date:	
Tested By:	

Pre-Hydrometer WC		
air dried mass + bowl	49.76	
M dry + bowl	49.71	
M bowl	39.35	
WC	#DIV/0!	

Mass of Sample used in Hydrometer		
As Tested Mass	65.51	201.83
Dry Mass	#DIV/0!	234.04
Gs	2.69	
Assumed/Measured	Assumed	

Hydrometer Analysis			
Hydrometer ID	350469		
j1	164.21		
j2	2.656		
Cm	0.25		
R0 at start	5.0	21 °C	Note: not necessary to remeasure unless Temp changes by
	5.0	21°C	

t (min)	Temp	R'h	R0	Rh	HR	nu	D
2	22.5	20.25		0.25	163.5460	1.7604	#DIV/0!
5	22.5	17.0		0.25	163.5460	1.7604	#DIV/0!
15	22.5	15		0.25	163.5460	1.7604	#DIV/0!
30	22.3	14		0.25	163.5460	1.7604	#DIV/0!
60	22.3	12.8		0.25	163.5460	1.7604	#DIV/0!
248	21.75	10.5		0.25	163.5460	1.7604	#DIV/0!
1440	21.5	9		0.25	163.5460	1.7604	#DIV/0!

(4:08)

Sieve size	mass	% retained	cum. % passing
2.36	0	#DIV/0!	#DIV/0!
1.18	0.24	#DIV/0!	#DIV/0!
0.6	0.08	#DIV/0!	#DIV/0!
0.425	0.04	#DIV/0!	#DIV/0!
0.3	0.07	#DIV/0!	#DIV/0!
0.212	0.19	#DIV/0!	#DIV/0!
0.15	5.23	#DIV/0!	#DIV/0!
0.075	22.39	#DIV/0!	#DIV/0!
0.063	3.25	#DIV/0!	#DIV/0!
total	0		
fines	#DIV/0!	#DIV/0!	

pan = 0.92

Summary

particle size	cum % passing
2.36	#DIV/0!
1.18	#DIV/0!
0.600	#DIV/0!
0.425	#DIV/0!
0.300	#DIV/0!
0.212	#DIV/0!
0.150	#DIV/0!
0.075	#DIV/0!
0.063	#DIV/0!
#DIV/0!	**#DIV/0!**
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!

Sample Name:	**Type C**
Depth:	
Date:	
Tested By:	

Pre-Hydrometer WC	E38
air dried mass + bowl	46.11
M dry + bowl	96.09
M bowl	38.49
WC	#DIV/0!

Mass of Sample used in Hydrometer		
As Tested Mass	65.51	178.56
Dry Mass	#DIV/0!	226.09
Gs	2.69	
Assumed/Measured	Assumed	

Hydrometer Analysis	
Hydrometer ID	350469
j1	164.21
j2	2.656
Cm	0.25
R0 at start	

Summary

particle size	cum % passing
2.36	#DIV/0!
1.18	#DIV/0!
0.600	#DIV/0!
0.425	#DIV/0!
0.300	#DIV/0!
0.212	#DIV/0!
0.150	#DIV/0!
0.075	#DIV/0!
0.063	#DIV/0!
#DIV/0!	**#DIV/0!**
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!

Note: not necessary to remeasure unless Temp changes by

t (min)	Temp	R'h (12)	R0	Rh	HR	nu	D
2	22.5	12		0.25	163.5460	1.7604	#DIV/0!
5	22.5	11		0.25	163.5460	1.7604	#DIV/0!
15	22.5	10		0.25	163.5460	1.7604	#DIV/0!
30	22.2	9.25		0.25	163.5460	1.7604	#DIV/0!
60	22.2	9		0.25	163.5460	1.7604	#DIV/0!
240	22	8		0.25	163.5460	1.7604	#DIV/0!
1440	21.5	7.5		0.25	163.5460	1.7604	#DIV/0!

Sieve size	mass	% retained	cum. % passing
2.36	0	#DIV/0!	#DIV/0!
1.18	0.11	#DIV/0!	#DIV/0!
0.6	0.13	#DIV/0!	#DIV/0!
0.425	0.19	#DIV/0!	#DIV/0!
0.3	0.89	#DIV/0!	#DIV/0!
0.212	6.40	#DIV/0!	#DIV/0!
0.15	19.78	#DIV/0!	#DIV/0!
0.075	17.01	#DIV/0!	#DIV/0!
0.063	2.09	#DIV/0!	#DIV/0!
total	0		
fines	#DIV/0!	#DIV/0!	

passed mass = 0.59g

NB: lost a bit of soil

Sample Name:	**Type D**
Depth:	
Date:	
Tested By:	

Summary

particle size	cum % passing
2.36	#DIV/0!
1.18	#DIV/0!
0.600	#DIV/0!
0.425	#DIV/0!
0.300	#DIV/0!
0.212	#DIV/0!
0.150	#DIV/0!
0.075	#DIV/0!
0.063	#DIV/0!
#DIV/0!	**#DIV/0!**
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!

Pre-Hydrometer WC

	D24
air dried mass + bowl	48.22
M dry + bowl	48.17
M bowl	39.00
WC	#DIV/0!

Mass of Sample used in Hydrometer

As Tested Mass	65.58	188.089
Dry Mass	#DIV/0!	219.00

Gs	2.69
Assumed/Measured	Assumed

Hydrometer Analysis

Hydrometer ID	350469
j1	164.21
j2	2.656
Cm	0.25
R0 at start	

Note: not necessary to remeasure unless Temp changes by

t (min)	Temp	R'h	R0	Rh	HR	nu	D
2	22	22		0.25	163.5460	1.7604	#DIV/0!
5	22	20.5		0.25	163.5460	1.7604	#DIV/0!
15	22	18		0.25	163.5460	1.7604	#DIV/0!
30	22	16		0.25	163.5460	1.7604	#DIV/0!
60	22	14.2		0.25	163.5460	1.7604	#DIV/0!
240	22	12		0.25	163.5460	1.7604	#DIV/0!
1440	21.5	10		0.25	163.5460	1.7604	#DIV/0!

4.76 0

Sieve size	mass	% retained	cum. % passing
2.36	0.05	#DIV/0!	#DIV/0!
1.18	0.09	#DIV/0!	#DIV/0!
0.6	0.22	#DIV/0!	#DIV/0!
0.425	0.14	#DIV/0!	#DIV/0!
0.3	0.34	#DIV/0!	#DIV/0!
0.212	1.14	#DIV/0!	#DIV/0!
0.15	11.32	#DIV/0!	#DIV/0!
0.075	15.53	#DIV/0!	#DIV/0!
0.063	1.93	#DIV/0!	#DIV/0!
total	0		
fines	#DIV/0!	#DIV/0!	

pan = 0.23

Sample Name: ~~WSD~~ Zeolite
Depth:
Date:
Tested By:

Pre-Hydrometer WC e12

air dried mass + bowl	41.50
M dry + bowl	41.36
M bowl	39.15
WC	#DIV/0!

Mass of Sample used in Hydrometer

As Tested Mass	~~65.84~~	221.47
Dry Mass + bowl	#DIV/0!	227.48

Gs	2.69
Assumed/Measured	Assumed

Hydrometer Analysis

Hydrometer ID	350469
j1	164.21
j2	2.656
Cm	0.25
R0 at start	

Note: not necessary to remeasure unless Temp changes by

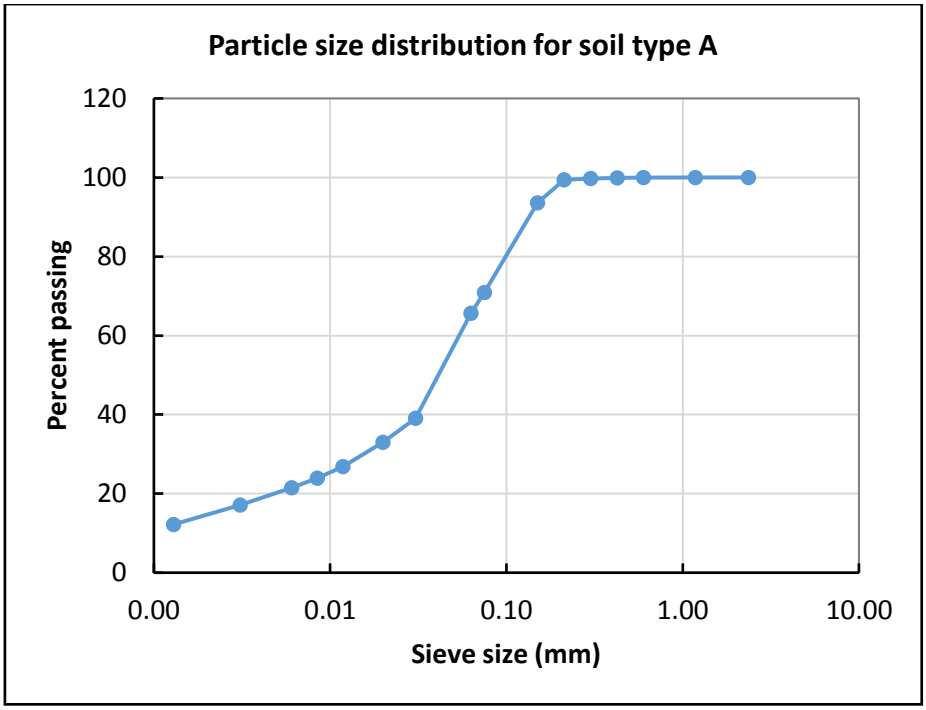
t (min)	Temp	R'h	R0	Rh	HR	nu	D
2	22	33		0.25	163.5460	1.7604	#DIV/0!
5	22	30.2		0.25	163.5460	1.7604	#DIV/0!
15	22	27.5		0.25	163.5460	1.7604	#DIV/0!
30	22	25.7		0.25	163.5460	1.7604	#DIV/0!
60	22	24		0.25	163.5460	1.7604	#DIV/0!
240	22	20		0.25	163.5460	1.7604	#DIV/0!
1440	21.5	15.5		0.25	163.5460	1.7604	#DIV/0!

Summary

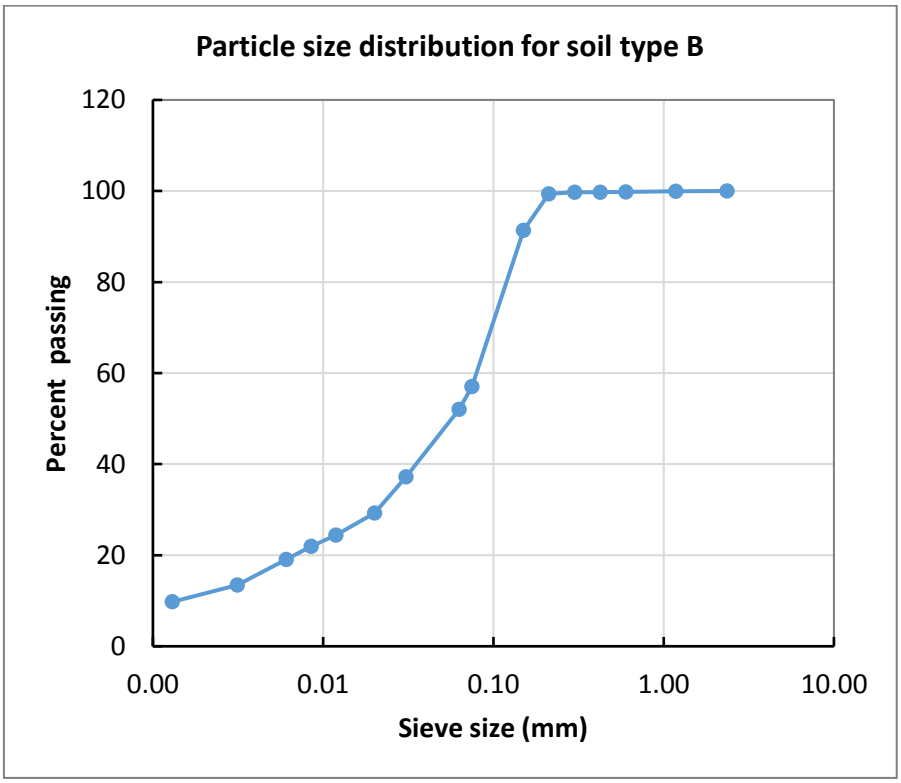
particle size	cum % passing
2.36	#DIV/0!
1.18	#DIV/0!
0.600	#DIV/0!
0.425	#DIV/0!
0.300	#DIV/0!
0.212	#DIV/0!
0.150	#DIV/0!
0.075	#DIV/0!
0.063	#DIV/0!
#DIV/0!	**#DIV/0!**
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!

Sieve size	mass	% retained	cum. % passing
2.36	0	#DIV/0!	#DIV/0!
1.18	0	#DIV/0!	#DIV/0!
0.6	0.01	#DIV/0!	#DIV/0!
0.425	0.05	#DIV/0!	#DIV/0!
0.3	0.04	#DIV/0!	#DIV/0!
0.212	0.21	#DIV/0!	#DIV/0!
0.15	0.73	#DIV/0!	#DIV/0!
0.075	3.74	#DIV/0!	#DIV/0!
0.063	1.45	#DIV/0!	#DIV/0!
total	0		
fines	#DIV/0!	#DIV/0!	

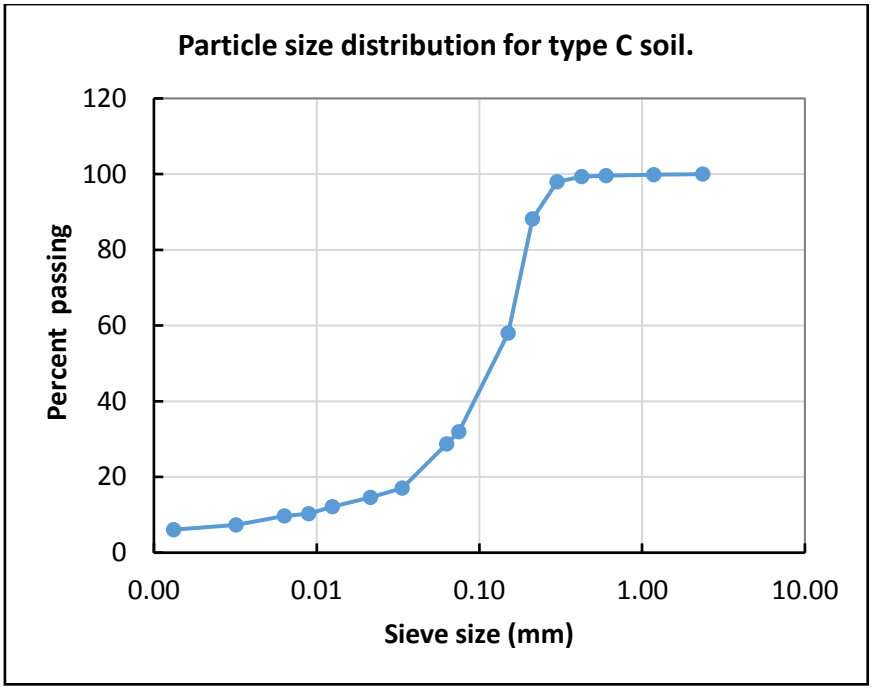
pan = 0.18



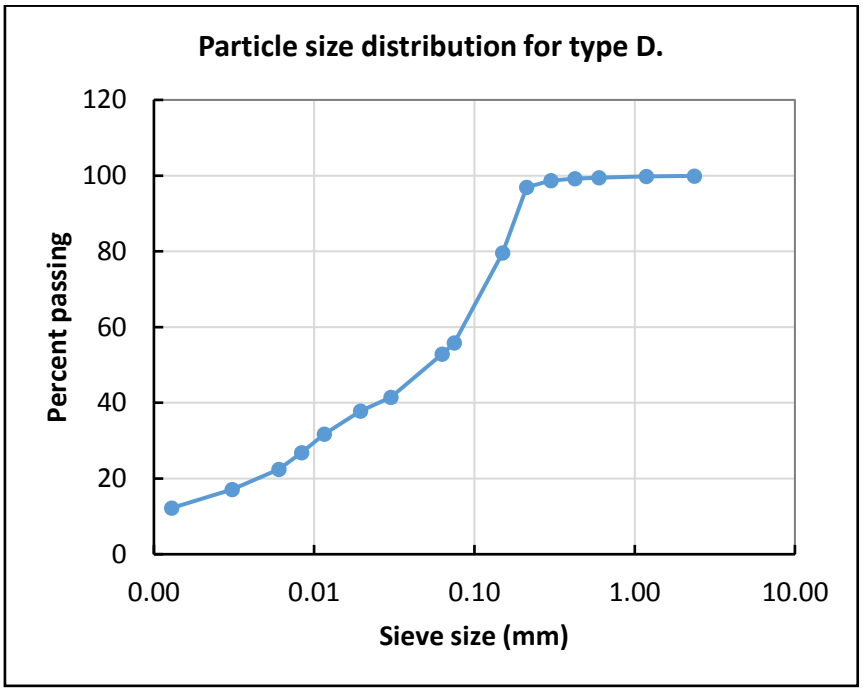
Particle size distribution curve of soil type A



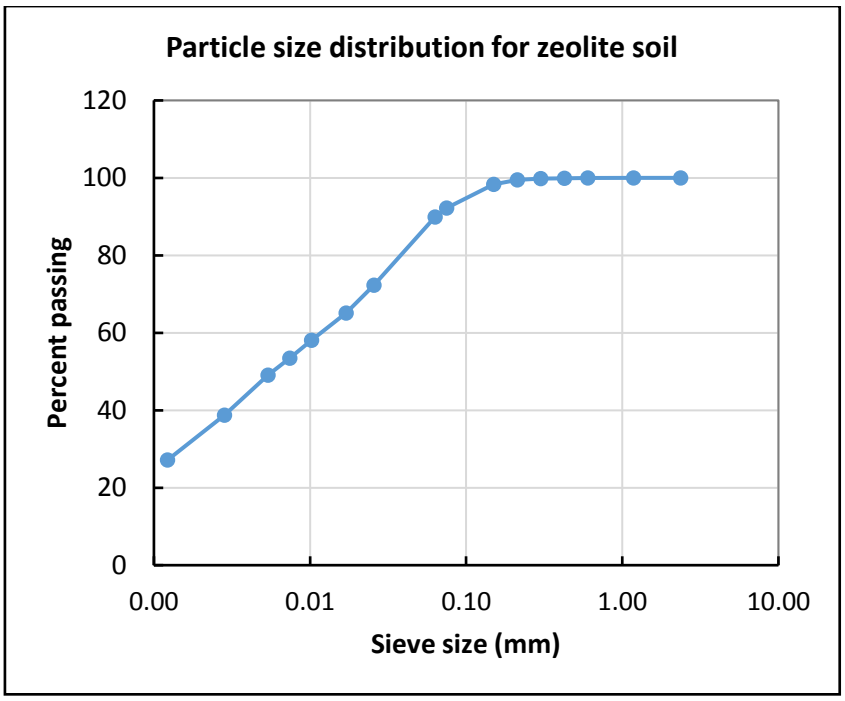
Particle size distribution curve of soil type B



Particle size distribution curve of type C soil.



Particle size distribution curve of soil type D.



Particle size distribution curve of zeolite

Appendix K : Adsorbent data sheets

Blue Pacific MINERALS

Zeolite - milled
Safety Data Sheet

1. Identification of Substance & Company

Product	
Product name	Zeolite - milled
Product code	to be advised
HSNO approval	HSR002512 or HSR002545
Approval description	Additives, Process Chemicals and Raw Materials (Toxic 6.7]) Group Standard 2006 or Construction Products (Toxic [6.7A]) Group Standard 2006
UN number	NA
Proper Shipping Name	NA
Packaging group	NA
Hazchem code	NA
Uses	Raw material
Company Details	
Company	**Blue Pacific Minerals**
Address	11-17 Huttloc Drive, Tokoroa 3420 New Zealand
Website	www.bpmnz.co.nz
Telephone	+64 7 885 0550
Email	info@bpmnz.co.nz

Emergency Telephone Number: +64 274 573007

2. Hazard Identification

Approval

This product has been approved under the Hazardous Substances and New Organisms Act (HSNO, Approval HSR002544 or HSR2503, Construction Products (Subsidiary Hazard) Group Standard 2006) or Additives, Process Chemicals and Raw Materials (Subsidiary Hazard) Group Standard 2006, and is classified as follows:

Classes	Hazard Statements
6.3A	Causes skin irritation.
6.4A	Causes eye irritation.
6.7A*	May cause cancer
6.9A*	Causes damage to organs through prolonged or repeated exposure

** This substance only triggers 6.7A and 6.9A if it is in the form of a fine respirable dust in an occupational (chronic exposure) setting.*

SYMBOLS

DANGER

Other Classifications

There are no other Classifications that are known to apply.

Precautionary Statements

Precautionary	Read label before use. Wash hands thoroughly after handling. Wear protective gloves/protective clothing. Wear eye/face protection. Obtain special instructions before use. Do not handle until all safety precautions have been read and understood. IF exposed or concerned: Get medical advice/ attention. Store locked up

IF ON SKIN: Wash with plenty of soap and water. If skin irritation occurs: get medical advice/attention. Take off contaminated clothing and wash before re-use.
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Apply continuous irrigation with water for at least 15 minutes holding eyelids apart. If eye irritation persists: Get medical advice.

3. Composition / Information on Ingredients

Component	CAS/ Identification	Conc (w/w %)
Zeolite – crystalline aluminosilicates may contains oxides including silica and aluminium oxide:	1318-02-1	100
Silica component may include		
Cristobalite	14464-46-1	<10
Quartz (crystalline silica)	14808-60-7	<10

This is a commercial product whose exact ratio of components may vary. Trace quantities of impurities are also likely.

4. First Aid

General Information

If medical advice is needed, have product container or label at hand. You should call the National Poisons Centre if you feel that you may have been poisoned, burned or irritated by this product. The number is 0800 764 766 (0800 POISON) (24 hr emergency service). IF exposed or concerned: Get medical advice/ attention.

Recommended first aid facilities: Ready access to running water is required. Accessible eyewash is required.

Exposure

Swallowed: Do NOT induce vomiting. Give a glass of water to drink. Contact a doctor.

Eye contact: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Apply continuous irrigation with water for at least 15 minutes holding eyelids apart. If eye irritation persists: Get medical advice.

Skin contact: IF ON SKIN: Wash with plenty of soap and water. If skin irritation occurs: get medical advice/attention. Take off contaminated clothing and wash before re-use.

Inhaled: IF INHALED: If breathing is difficult, remove to fresh air and keep at rest in a position comfortable for breathing. If patient is unconscious, place in the recovery position (on the side) for transport and contact a doctor. If experiencing respiratory symptoms: Immediately call a POISON CENTER or doctor/physician.

Advice to Doctor

Treat symptomatically

5. Firefighting Measures

Fire and explosion hazards: There are no specific risks for fire/explosion for this chemical. It is non-flammable.

Suitable extinguishing substances: Carbon dioxide, extinguishing powder or water jet. Fight larger fires with water jet or alcohol resistant foam.

Unsuitable extinguishing substances: Unknown.

Products of combustion: Product does not burn. Dust may form irritating atmosphere.

Protective equipment: No special measures are required.

Hazchem code: NA

6. Accidental Release Measures

Containment: If greater than 1000kg is stored, secondary containment is required. Emergency plans to manage any potential spills must be in place. Prevent spillage from spreading or entering soil, waterways or drains.

Emergency procedures: In the event of large spillage (>100kg) of the dry product alert the fire brigade to location and give brief description of hazard.
Wear protective equipment to prevent skin, eye and respiratory exposure. Clear area of any unprotected personnel. Contain spill. Prevent by whatever means possible any spillage from entering drains, sewers, or water courses.

Clean-up method	Collect product avoiding any dust formation, and seal in properly labelled containers or drums for disposal. If contamination of crops, sewers or waterways has occurred advise local emergency services.
Disposal	Vacuum up and collect recoverable material into labelled containers for recycling or salvage. Recycle containers wherever possible. This material may be suitable for approved landfill. Dispose of only in accord with all regulations.
Precautions	Wear protective equipment to prevent skin and eye contamination and the inhalation of dust. Work up wind or increase ventilation.

7. Storage & Handling

Storage	Stable under normal use and storage conditions.
Handling	Keep exposure to a minimum, and minimise the quantities kept in work areas. See section 8 with regard to personal protective equipment requirements. Do not breathe dust.

8. Exposure Controls / Personal Protective Equipment

Workplace Exposure Standards

A workplace exposure standard (WES) has not been established by WorkSafe NZ for this product. There is a general limit of 10mg/m^3 for dusts and mists when limits have not otherwise been established.

NZ Workplace Exposure Stds (2013)	Ingredient	WES-TWA	WES-STEL
	Silicon dioxide	see crystalline silica	data unavailable
	Aluminium oxide	10mg/m^3	data unavailable
	Iron (II) Oxide	5mg/m^3 (as Fe)	data unavailable
	Magnesium oxide	10mg/m^3 (fume)	data unavailable
	Calcium oxide	2mg/m^3	data unavailable
	Titanium dioxide	10mg/m^3	data unavailable
	Quartz (SiO_2):		
	quartz, respirable dust	0.2mg/m^3	data unavailable
	cristobalite, respirable dust	0.1mg/m^3	data unavailable

Engineering Controls

In industrial situations, it is expected that employee exposure to hazardous substances will be controlled to a level as far below the WES as practicable by applying the hierarchy of control required by the Health and Safety in Employment Act 1992 (HSE). Exposure can be reduced by process modification, use of local exhaust ventilation, capturing substances at the source, or other methods. If you believe air borne concentrations of mists, dusts or vapours are high, you are advised to modify processes or increase ventilation.

Personal Protective Equipment

Eyes	Protective eyewear is not normally necessary when using this product. However, it always prudent to use protective eyewear if dust is likely.
Skin	Avoid repeated or prolonged skin contact. Wear overalls, rubber boots and impervious gloves. Replace frequently. Gloves should be checked for tears or holes before use. Remove protective clothing and wash exposed areas with soap and water prior to eating, drinking or smoking. Wash contaminated clothing before re-use.
Respiratory	 Use of a P2 dust mask or fine particulate half or full face respirator with an effective seal is recommended when airborne concentrations approach the WES (section 8). Fit testing and clear guidelines and training for use and maintenance of PPE are necessary.

WES Additional Information

Not applicable

9. Physical & Chemical Properties

Appearance	fine dust, off white/tan colour
Odour	no odour
pH	8.65 (10% aqueous suspension)
Vapour pressure	NA
Viscosity	NA
Boiling point	NA
Volatile materials	no data
Freezing / melting point	NA
Solubility	not soluble in water
Specific gravity / density	~0.65g/cm^3
Flash point	no data
Danger of explosion	NA
Auto-ignition temperature	NA
Upper & lower flammable limits	NA
Corrosiveness	non corrosive

10. Stability & Reactivity

Stability	Stable
Conditions to be avoided	Containers should be kept closed in order to avoid contamination. Avoid the creation of dust.
Incompatible groups	Avoid contact with strong oxidsing agents and hydrogen fluoride.
Hazardous decomposition products	None known
Hazardous reactions	Zeolites will react with hydrogen fluoride (HF) acid. Avoid contact with strong oxidsing agents.

11. Toxicological Information

Summary

IF IN EYES: Fine dust may cause irritation when in direct contact.

IF ON SKIN: Material may cause drying out of skin.

IF INHALED: May cause respiratory irritation. Also see chronic effects.

IF SWALLOWED: No adverse effects anticipated under normal use conditions.

CHRONIC EFFECTS: The adverse health effects from respirable crystalline silica exposure-silicosis, cancer, scleroderma, tuberculosis, and nephrotoxicity- are chronic effects.

Supporting Data

Acute	**Oral**	Not considered acutely toxic if swallowed.
	Dermal	Not considered acutely toxic by dermal contact.
	Inhaled	The substance is not considered acutely toxic if inhaled, however there may be irritation of the respiratory tract if dust is inhaled. Short term (acute) silicosis (see "systemic" below) can also occur with one-off exposures to extremely high levels of fine crystalline silica dust. Other short term effects include irritation, choking and difficulty breathing.
	Eye	The mixture is not considered to be an eye irritant. Dust may be an eye irritant (mechanical irritation).
	Skin	The mixture is considered to be a mild skin irritant.
Chronic	**Sensitisation**	No ingredient present at concentrations > 0.1% is considered a sensitizer.
	Mutagenicity	No ingredient present at concentrations > 0.1% is considered a mutagen.
	Carcinogenicity	Zeolites have been classed by IARC as group 3 – cannot be evaluated as to their carcinogenicity to humans. However, there is evidence that this material does contain quartz and cristobalite. Crystalline silica inhaled in the form of quartz or cristobalite from occupational sources is carcinogenic to humans (IARC Group 1). Crystalline Silica triggers 6.7A classification (confirmed carcinogen). The carcinogenicity of silica is related to long term (e.g., 10 years) inhalation of very fine particulate. Carcinogenicity of silica appears linked to development of silicosis (see systematic below) followed by complications and, eventually lung cancer
	Reproductive / Developmental	No ingredient present at concentrations > 0.1% is considered a reproductive or developmental toxicant or have any effects on or via lactation.
	Systemic	The respirable fraction of this product is considered to be a target organ toxicant,

	because of the presence of crystalline silica at greater than 1%. Crystalline silica triggers 6.9A classification if it is in the form of a fine respirable dust in an occupational (chronic exposure) setting. This is due to the development of silicosis which can occur following exposure to extremely high levels of fine silica dust. Silicosis is a type of pneumoconiosis – a disease of the lung that causes inflammation, scar tissue, lesions and fibrosis in the lung (alveolar). Symptoms include shortness of breath, cough, fever, loss of appetite and cyanosis (bluish skin). Silicosis can occur following prolonged exposure (e.g., 10 years) to relatively high levels of fine crystalline silica dust.
Aggravation of existing conditions	None known

12. Ecological Data

Summary

This product is not considered ecotoxic.

Supporting Data

Aquatic	Not ecotoxic in the aquatic environment.
Bioaccumulation	No data
Degradability	No data
Soil	No consided ecotoxic in the soil environment.
Terrestrial vertebrate	Not toxic towards terrestrial vertebrates
Terrestrial invertebrate	Not toxic towards terrestrial invertebrates
Biocidal	Not biocidal
Environmental effect levels	No EELs are available for this mixture or ingredients

13. Disposal Considerations

Restrictions	There are no product-specific restrictions, however, local council and resource consent conditions may apply, including requirements of trade waste consents.
Disposal method	Disposal of this product must comply with the requirements of the Resource Management Act for which approval should be sought from the Regional Authority. The substance must be treated and therefore rendered non-hazardous before discharge to the environment.
Contaminated packaging	Rinse containers with water before disposal. Preferably re-cycle container, otherwise send to landfill or similar.

14. Transport Information

There are no specific restrictions for this product (not a dangerous good).

UN number:	NA	**Proper shipping name:**	NA
Class(es)	NA	**Packing group:**	NA
Precautions:	Not applicable.	**Hazchem code:**	NA

15. Regulatory Information

This product is an approved substance under the Hazardous Substances and New Organisms Act (HSNO). Approval code: HSR002545 or HSR002512, Construction Products (Toxic 6.7) Group Standard 2006 or Additives, Process Chemicals and Raw Materials (Toxic 6.7) Group Standard 2006.

Specific Workplace Controls (as per HSNO approval referenced to Controls Matrix)

Key workplace requirements are:	
SDS	To be available within 10 minutes in workplaces storing > 50kg.
Labelling	No removal of labels and/or decanting of product into other containers can occur.
Emergency plan	Required if > 1000kg is stored.
Approved handler	Required if using or storing >10kg as a raw material. Not required if used as a construction product (exempt under the group standard HSR002545)
Tracking	Not required.
Bunding & secondary containment	Required if > 1000kg is stored.
Signage	Not required.
Location test certificate	Not required.
Flammable zone	Not required.
Fire extinguisher	Not required.

Note: The above workplace requirements apply if only this particular substance is present. The complete set of controls for a location will depend on the classification and total quantities of other substances present in that location.

Other Legislation

In New Zealand, the use of this product may come under the Resource Management Act and Regulations, the Health, Safety in Employment Act and Regulations, local Council Rules and Regional Council Plans.

16. Other Information

Abbreviations

Approval Code	Approval HSR002544 or HSR002503, Construction Products (Subsidiary Hazard) Group Standard 2006 or Additives, Process Chemicals and Raw Materials (Subsidiary Hazard) Group Standard 2006, Controls, EPA. www.epa.govt.nz
CAS Number	Unique Chemical Abstracts Service Registry Number
Ceiling	Ceiling Exposure Value: The maximum airborne concentration of a biological or chemical agent to which a worker may be exposed at any time.
Controls Matrix	List of default controls linking regulation numbers to Matrix code (e.g. T1, I16).
EC_{50}	Ecotoxic Concentration 50% – concentration in water which is fatal to 50% of a test population (e.g. daphnia, fish species)
ERMA	Environmental Risk Management Authority (now EPA)
EPA	Environmental Protection Agency (previously known as ERMA)
HAZCHEM Code	Emergency action code of numbers and letters that provide information to emergency services, especially fire fighters
HSNO	Hazardous Substances and New Organisms (Act and Regulations)
IARC	International Agency for Research on Cancer
LEL	Lower Explosive Limit
LD_{50}	Lethal Dose 50% – dose which is fatal to 50% of a test population (usually rats).
LC_{50}	Lethal Concentration 50% – concentration in air which is fatal to 50% of a test population (usually rats)
MSDS (SDS)	Material Safety Data Sheet (or Safety Data Sheet)
STEL	Short Term Exposure Limit - The maximum airborne concentration of a chemical or biological agent to which a worker may be exposed in any 15 minute period, provided the TWA is not exceeded
TWA	Time Weighted Average – generally referred to WES averaged over typical work day (usually 8 hours)
UEL	Upper Explosive Limit
UN Number	United Nations Number
WES	Workplace Exposure Standard - The airborne concentration of a biological or chemical agent to which a worker may be exposed.

References

Data	Unless otherwise stated comes from the EPA HSNO chemical classification information database (CCID) http://www.epa.govt.nz/hs/compliance/chemicals.html , for specific chemicals.
EPA Transfer Gazettes	Classifications and controls assigned for specific ingredients (consolidated gazette, 2004)
Controls Matrix	Part of the EPA New Zealand User Guide to the HSNO Control Regulations
WES 2013	The NZ Workplace Exposure Standards Effective from 2013, published by WorkSafe NZ and available on their web site – www.worksafe.govt.nz.
Other References:	Suppliers SDS

Review

Date	**Reason for review**
April 2016	New SDS.

Disclaimer

Appendix L : Adsorption raw data and summary results from first and second batch.

Batch	Sample/sorbate	pH	Adsorbent	Dosage (mg/L)	Shaking Time (hours)	Mixing Speed (rpm)	Settling Time (minutes)	Initial NH_4 (mg/L)	Final NH_4 (mg/L)	NH_4 adsorption (mg/g)	NH_4 removal (%)
1st	Leachate sample	≈6	Zeolite - NZ	50,000	4	350–400	30	2124	1703	8.42	19.0
			Zeolite - NZ	50,000	4	350–400	90	2124	1630	9.89	23.0
			Type A	50,000	22	350–400	30	2124	2040	1.67	3.97
			Type B	50,000	22	350–400	30	2124	2046	1.57	3.7
			WSD Silt	50,000	22	350–400	90	2124	2111	0.26	0.6
			Silt Dam	50,000	22	350–400	90	2124	2055	1.38	3.3
2nd	Leachate Sample A	≈6	Zeolite - NZ	50,000	6	350–400	90	2152	1629	10.4	24.3
	Leachate Sample B		Zeolite - NZ	50,000	6	350–400	90	2049	1522	10.5	25.8
	Leachate Sample C		Zeolite - NZ	50,000	6	350–400	90	2065	1544	10.4	25.2

Appendix M : Summary results of second batch experiments.

Day	Time (days)	NH_4 (mg/L)	NH_4 @ Feed (mg/L)	NH_4-N ($mgNL^{-1}$)	NO_3 (mg/L)	NO_3 @ Feed (mg/L)	NO_3-N ($mgNL^{-1}$)	COD (mg/L)	COD @ Feed (mg/L)
Friday	1	200		156	8.2		1.85	1019	
Sunday	3	216		168	8.3		1.87	708	
Monday	4	231	265	180	1.5	5.8	0.34	633	590
Wednesday	6	269		209	3		0.68	524	
Friday	8	281	284	219	2.4	1.2	0.54	646	695
Wednesday	6	231		180	3.3		0.75	541.25	
Wednesday	7	231	259	180	8.3	1.7	1.87	486.25	506.25
Thursday	8	226		176	22.4		5.06	437.5	
Friday	9	196		152	35		7.90	283	
Saturday	10	113	104	88	52	52	11.74	75	
Sunday	11	80		62	117		26.42	17	
Monday	12	80		62	141		31.84	35	
Tuesday	13	88		68	306		69.10	463	
Wednesday	14	98	112	76	117	28	26.42	396	426
Thursday	15	61		47	115		25.97	185	
Friday	16	63		49	116		26.19	140	
Saturday	17	65	88	51	139	33	31.39	208	315
Sunday	18	55		43	122		27.55	201	
Monday	19	57		44	135		30.48	178	
Tuesday	20	66	95	51	163	31	36.81	180	248
Wednesday	21	58		45	153		34.55	235	
Thursday	22	50		39	98		22.13	391	
Friday	23	60	153	47	97	11	21.90	289	415
Saturday	24	101		79	74		16.71	250	400
Sunday	25	93		72	93		21.00	289	
Monday	26	93	177	72	175	44	39.52	290	390
Tuesday	27	114		89	172		38.84	250	
Wednesday	28	124		96	209		47.19	488	
Thursday	29	133	196	103	333	64	75.19	323	549
Friday	30	132		103	99		22.35	660	
Saturday	31	141		110	103		23.26	1040	
Sunday	32	143		111	127		28.68	860	
Monday	33	146		114	166		37.48	694	
Tuesday	34	154		120	236		53.29	583	
Wednesday	35	165	225	128	287	46	64.81	561	566
Thursday	36	173		135	121		27.32	456	
Friday	37	142		110	195		44.03	330	
Saturday	38	152		118	257		58.03	283	

Appendix N : Some of the raw data of second batch experiments.

Test No.	Sampling No.	Date	Day	Time	Time (min)	Time (h)	Parameter measured								Volume (ml)
							pH	Dissolved Oxygen (mg/L)	Conductivity (mg/L)	NH_3-N (mg/L)	NO_3 - N (mg/L)	COD (mg/L)	MLSS (mg/L)	MLVSS (mg/L)	
							No Feed (sludge + water)								
1	R1	Friday	Day 1	10:00AM	5	0	6.89	0.19	731	16	12	110	2520	2890	2000
				12:00PM		2	7.03	0.05	737	-	-	-	-	-	1945
				1:00PM		5	7.14	0.04	743	-	-	-	-	-	
				2:00PM		7	7.22	0.03	745	-	-	-	-	-	
				4:00PM		9	7.29	0.02	755	-	-		-	-	
				6:00 PM		11	7.35	0.02	758	-	-	-	-	-	
				8:00 PM		13	7.37	0.05	776	-	-		-	-	
				11:00 PM		16	7.46	0.15	770	-	-	-	-	-	
	R2			10:00AM	5	0	6.89	0.23	703	24	16	130	2480	3246	2000
				12:00PM		2	7.03	0.08	708	-	-	-	-	-	1945
				1:00PM		5	7.14	0.4	719	-	-	-	-	-	
				2:00PM		7	7.22	0.03	728	-	-	-	-	-	
				4:00PM		9	7.29	0.02	745	-	-		-	-	
				6:00 PM		11	7.35	0.02	764	-	-	-	-	-	
				8:00 PM		13	7.37	0.02	784	-	-		-	-	
				11:00 PM		16	7.46	0.02	793	-	-	-	-	-	
	R1	Saturday	Day 2	10:00AM		24	7.45	0.94	770	35	25	155	-	-	1905
				3:00PM		29	7.65	0.15	884	-	-	-	-	-	

1				5:00PM		31	7.65	2.79	891.0	-	-	-	-	-	
				7:00PM		33	7.81	3.89	856	-	-	-	-	-	
	R2			10:00AM		24	7.3	0.16	851	47	20	213	-	-	1905
				3:00PM		29	7.34	0.08	848	-	-	-	-	-	
				5:00PM		31	7.39	0.05	923	-	-	-	-	-	
				7:00PM		33	7.46	0.2	923	-	-	-	-	-	
	R1	Sunday	Day 3	12:00PM		45	7.39	0.1	920	-	-	-	-	-	
				2:00PM		47	7.43	0.02	723	-	-	-	-	-	
				4:00PM		49	7.01	0.02	749	-	-	-	-	-	
				6:00 PM		51	6.64	4.89	811	-	-	-	-	-	
	R2			12:00PM		45	7.76	5.91	914	-	-	-	-	-	
				2:00PM		47	7.71	5.71	930	-	-	-	-	-	
				4:00PM		49	7.7	5.89	921	-	-	-	-	-	
				6:00 PM		51	7.65	5.21	910	-	-	-	-	-	
	R1	Monday	Day 4	12:00PM		69	621	0.2	830	28	119	113	-	-	1800
				2:00PM		71	6.22	0.18	873	-	-	-	-	-	
				4:00PM		73	6.2	0.14	885	-	-	-	-	-	
				6:00 PM	5	75	6.1	6	1088	-	-	-	-	-	
				10:00PM		79	6.02	6.03	1100	-	-	-	-	-	
	R2			12:00PM		69	6.58	6.48	953	25	78	230	-	-	1850
				2:00PM		71	6.54	6.44	956	-	-	-	-	-	
				4:00PM		73	6.3	6.47	980	-	-	-	-	-	
				6:00 PM		75	6.31	6.42	1005	-	-	-	-	-	
				10:00PM		79	6.33	5.61	1015	-	-	-	-	-	
	R1	Wednesday	Day 6	10:00AM		115	6.32	0.02	-	33	112	105	-	-	1700
				1:00PM		118	6.21	0.02	-	-	-	-	-	-	
	R2			10:00AM		115	6.35	3.92	1177	30	98	188	-	-	1780
				1:00PM		118	6.33	4.22	1181	-	-	-	-	-	

2	R1	Friday Before Feed	Day 7	-	-	-	-	-	-	25	118	168	-	-	1660
	R2			-	-	-	-	-	-	18	112	198	-	-	1720
		Friday After Feed		**Feed 1**											
	R1			5:00PM	5	147	6.8	6.52	1110	64	85	175	1260	1880	1600
				7:00PM		149	7.3	6.01	1561	-	-	-	-	-	2000
				10:00PM		152	7.02	5.91	1653	-	-	-	-	-	
	R2			5:00PM		147	6.9	5.44	1686	54	65	213	1180	1800	1600
				7:00PM		149	7.28	6.12	1203	-	-	-	-	-	2000
				10:00PM		152	7.4	4.9	1666	-	-	-	-	-	
	R1	Sunday	Day 9	6:00 PM	5	168	5.06	5.58	1811	60	105	180	-	-	1900
				8:00 PM		170	5.09	6.1	1917	-	-	-	-	-	
	R2			6:00 PM		168	5.86	5.44	1686	38	78	233	-	-	1900
				8:00 PM		170	5.71	5.69	1673	-	-	-	-	-	-
3				**Feed 2**											
	R1	Wednesday Before Feed	Day 12	2:00PM		234	-	-	-	70	144	105	940	1760	1600
	R2			2:00PM		234	-	-	-	39	174	172	640	1540	1550
	R1	Wednesday Before Feed	Day 12	3:00PM	5	235	621	0.2	830	102	116	145	940	1700	1600
				5:00PM		237	6.22	0.18	873	-	-	-	-	-	2000
				7:00PM		239	6.2	0.14	885	-	-	-	-	-	
	R2			3:00PM		235	6.58	6.48	953	85	116	278	1020	1700	1550
				5:00PM		237	6.54	6.44	956	-	-	-	-	-	2000
				7:00PM		239	6.3	6.47	980	-	-	-	-	-	
	R1	Thursday	Day 13	12:00PM		256	5.97	5.94	2526	-	-	-	-	-	-
				1:00PM		257	5.89	5.92	2500	-	-	-	-	-	-
				3:00PM		259	5.72	5.98	2521	-	-	-	-	-	-

4				7:00PM		263	5.55	6.08	2548	-	-	-	-	-	-
	R2			12:00PM		256	6.61	3.77	2059	-	-	-	-	-	-
				1:00PM		257	6.43	3.84	2055	-	-	-	-	-	-
				3:00PM		259	6.02	4.92	2049	-	-	-	-	-	-
				5:00PM		261	5.09	5.24	2040	-	-	-	-	-	-
				7:00PM		263	5.89	5.82	2035	-	-	-	-	-	-
	R1	Friday	Day 14	10:00AM		278	5.23	6.19	2642	-	-	-	-	-	-
				12:00PM		280	5.23	6.14	2640						
				1:00PM		281	5.23	6.04	2649	-	-	-	-	-	-
				3:00PM		283	5.23	6.04	2654	-	-	-	-	-	-
				5:00PM		285	5.24	6.04	2678	-	-	-	-	-	-
				7:00PM		287	5.27	6.08	2700	-	-	-	-	-	-
	R2			10:00AM		278	5.33	6.22	1964	-	-	-	-	-	-
				12:00PM		280	5.29	6.12	1961						
				1:00PM		281	5.27	6.22	1946	-	-	-	-	-	-
				3:00PM		283	5.26	6.04	1940	-	-	-	-	-	-
				5:00PM		285	5.27	5.72	1944	-	-	-	-	-	-
				7:00PM		287	5.27	5.71	2035	-	-	-	-	-	-
	R1	Sunday	Day 16	5:00PM		330	5.37	5.59	3010	53	284	140	-	-	1450
				7:00PM		333	5.18	6.16	2978	-	-	-	-	-	-
	R2			5:00PM		330	5.13	6.01	2491	110	142	X	-	-	1450
				7:00PM		333	5.22	6.38	2519				-	-	
	R1	Monday	Day 17	3:00PM		354	5.18	2.78	2564	-	-	-	-	-	-
				5:00PM		356	5.24	3.49	2576				-	-	
				7:00PM		358	5.25	3.22	2588	60	194	X	-	-	1400
	R2			3:00PM		354	5.29	6.02	3024	-	-	-	-	-	-

				5:00PM		356	5.24	5.92	3074	-	-	-	-	-	-
4				7:00PM		358	5.17	5.91	3079	124	164	208	-	-	1400
	R1			**Feed 3**											
				09:00PM		360	5.16	6.28	3163	133	134	315	X	X	1400
				10:00PM		361	6.3	6.3	2941	-	-	-	-	-	-
	R2			09:00PM		360	5.22	4.48	2555	105	182	X	X	X	1400
				10:00PM		361	6.86	6.23	2653	-	-	-	-	-	-
	R1	Tuesday	Day 18	3:00PM		378	7.06	5.76	2979	-	-	-	-	-	-
				5:00PM		380	6.69	5.86	2987						
				7:00PM		382	6.61	5.79	2998	-	-	-	-	-	-
				8:00PM		384	5.23	6.04	2654	-	-	-	-	-	-
				10:00PM		386	5.24	6.04	2678	-	-	-	-	-	-
	R2			3:00PM		378	7.07	2.3	1858	-	-	-	-	-	-
				5:00PM		380	6.95	1.78	1822	-	-	-	-	-	-
				7:00PM		382	6.88	1.35	1813						
				8:00PM		384	5.27	6.22	1946	-	-	-	-	-	-
				10:00PM		386	5.26	6.04	1940	-	-	-	-	-	-